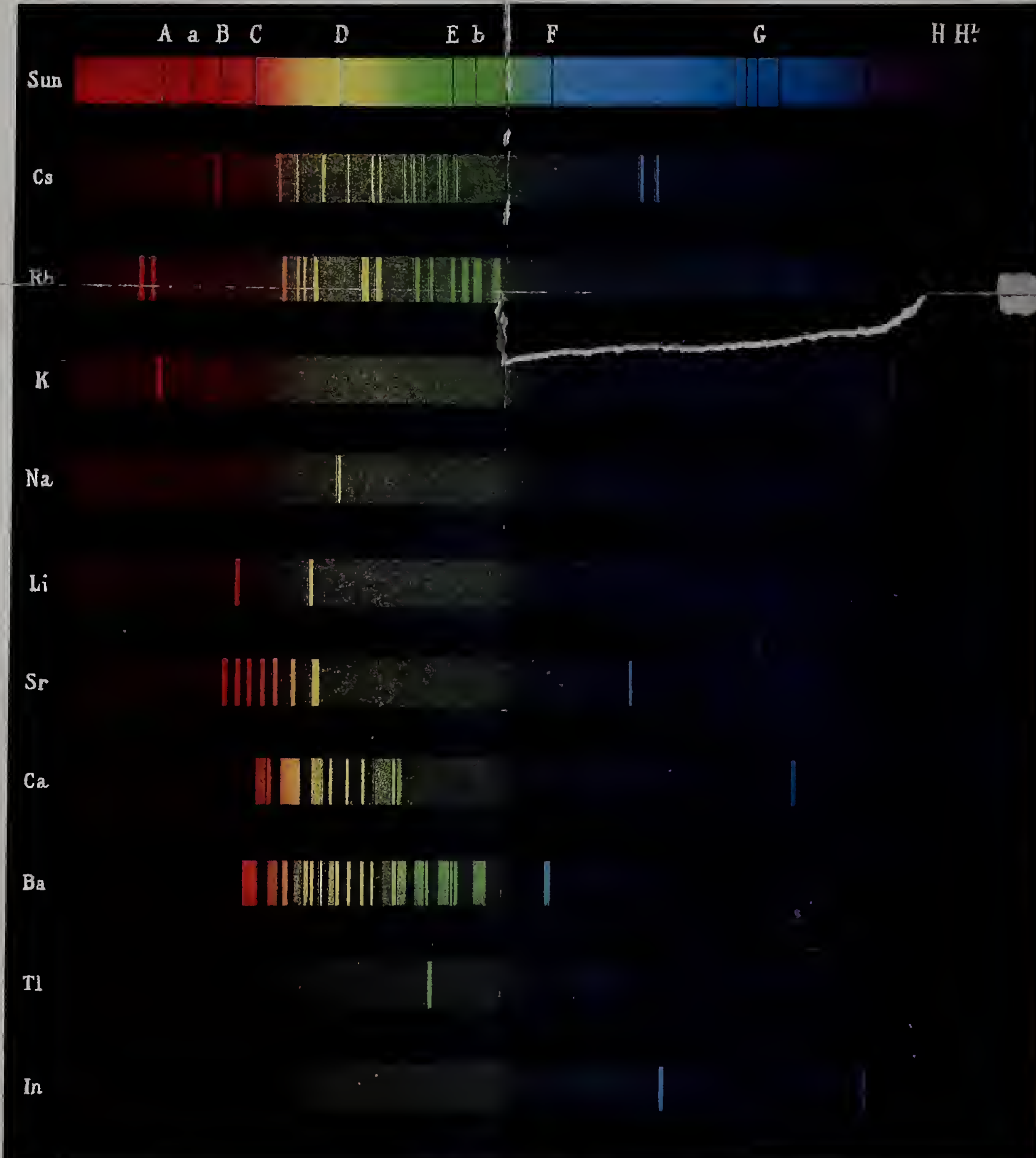
A MANUAL OF CHEMISTRY



HANHART LITH.

A

MANUAL OF CHEMISTRY

THEORETICAL AND PRACTICAL

(BASED ON WATTS' EDITION OF FOWNES' MANUAL)

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PREFACE.

The production of this work may be briefly explained as follows. The publishers having requested me to revise once more the Manual which had been prepared by the late Mr Henry Watts, on the basis of Fownes, a careful examination of the book showed that it would be necessary to rewrite a large part of the existing matter and to add a considerable amount of new. The last traces of the work of Fownes have disappeared in the process. Hence, although the general arrangement of the contents is similar to that of the original, we have now a practically new book, in which the phraseology as well as the matter has been modernised. A preliminary chapter has been added, in which a survey of the most important events in the development of Chemistry, from the time of Boyle, has been attempted. I have found such a historical survey to constitute a useful introduction to the general study of the science. Many additional illustrations have also been introduced.

This book is not intended for children, neither is it suited to the requirements of the most advanced students. It aims at presenting in a compact form a body of facts and a statement of the leading doctrines of Modern Chemistry, suitable to the needs of students who are receiving instruction

under a teacher, and who require a Manual to which they can resort for the purpose of verifying and extending such information as they receive in the lecture-room. Directions are also provided for carrying out a number of simple experiments such as every student ought to perform with his own hands. These, however, must be looked upon only as suggestive, and can easily be multiplied, extended, or modified according to the judgment of the teacher. While studying the non-metallic elements, students should learn the usual analytical tests by which the common acids are recognised, those for the metals being taken later. This is a reversal of the usual order, though more natural.

In the table of contents those portions which may be omitted at first are indicated by a star.

The order in which the elements are taken for study may not commend itself to those Chemists who look upon the periodic system as a final scheme of classification. But, without entering into a discussion of this question, my experience leads me to believe that a rigid adherence to the order in which the elements follow one another in that system is a continual source of difficulty, alike to teachers and students. I prefer, for teaching purposes at any rate, an arrangement of groups, the members of which stand in obviously natural relationship to one another, and, independently of mere considerations of valency, do as a matter of fact closely resemble each other. This does not prevent the teacher from directing careful attention to the important principle which underlies the periodic system.

It is scarcely to be expected that a book which contains so large a number of figures and formulæ should be entirely free from errors, but great care has been given to the correc-

tion of the proofs, and all new data have been taken directly from original sources.

For the excellent index with which the volume is provided, I am indebted to the friendly assistance of Miss Edith Ayrton.

ROYAL COLLEGE OF SCIENCE,
LONDON, *February* 1897.

DIRECTIONS TO THE STUDENT.

Paragraphs headed "Experiment" contain instructions for the performance of simple operations, which you should carry out for yourself. Do not be satisfied with half-finishing these experiments. If not entirely successful, seek for help from your teacher. Articles indicated in the Table of Contents by a star may be omitted on first reading the book.

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PLATE.—CURVE OF ATOMIC VOLUMES, ETC.

ERRATA.

Page 39, line 7 from bottom, *for* 1·2505 *read* 1·2511.
,, 49, footnote, *for* viii. *read* iii.
,, 51, line 5 from top, *after* sulphur *add* dioxide.
,, 156, ,, 3 ,, *for* of *read* or.
,, 195, ,, 10 ,, equation should be—
$CaC_2 + 2H_2O = Ca(HO)_2 + C_2H_2$.
,, 219, ,, 23 ,, *after* unknown *insert* in a definite state.
after but *insert* the various forms of hydrated gelatinous silica consist of mixtures of these acids and
,, 266, ,, 15 ,, *for* Mendelejeff *read* Mendeléeff.
,, 268, *for* La 133 *read* La 138.
,, 271, ,, 20 ,, *for* Mendelejeff *read* Mendeléeff.
,, 343, ,, 16 ,, *for* 110 *read* 115.
,, 370, ,, 7 from bottom, *for* Ca *read* Cs.
,, 416, ,, 8 from top, *for* aluminum *read* aluminium.
,, ,, ,, 16 ,, *for* dichlorides *read* lower chlorides.
,, 448, ,, 7 from bottom, *for* Mendelejeff *read* Mendeléeff.
,, 463, ,, 5 ,, ,, ,, ,, ,,
,, 477, ,, 11 ,, *for* clay-iron stone *read* clay ironstone.

A

MANUAL OF CHEMISTRY.

INTRODUCTION.

THE Science of Chemistry has for its object the study of the composition of the materials out of which are formed the earth, the sea, the air, and the organised and living beings which inhabit them. Chemistry also seeks to explain the connection between the composition of bodies and their properties.*

In ordinary scientific speech the term *chemical* is applied to changes which permanently affect the properties or characters of bodies, in opposition to effects termed *physical*, which are not attended by such consequences. Changes of composition or combination are thus easily distinguished from those temporarily brought about by heat, electricity, magnetism, and mechanical force, whose laws and effects lie within the province of Physics.

The foundation of modern opinions concerning the nature of matter and the relation of a compound to its constituents was laid by Robert Boyle (born 1627, died 1691) and his disciples Hooke and Mayow. Many chemical arts, such as the working of several metals, the production of glass, soap, and some dyes, and the distillation of alcohol from fermented liquids, had been practised from very early times. Evidence of the antiquity of such processes is afforded by references to them in the Old Testament, and by the dyes found in the mummy cloths of Egypt. The early history of these arts and of the first notions as to the nature of matter which may have arisen in connection with them is entirely unknown to us now, but such words as *alkali*, *alcohol*, and *alchemy*, are evidently of Arabic origin. Alchemy, and hence Chemistry, has been derived from the word *Kemia*, a native name of Egypt, also signifying black; hence Alchemy was the black or Egyptian art. The ancient doctrine Alchemy.

* Compare Scheele's definition :—"It is the object and chief business of Chemistry to skilfully separate substances into their constituents, to discover their properties, and to compound them in different ways."

attributed to Aristotle, taught the fundamental unity of all matter, but ascribed its different forms to the possession of certain qualities typified by fire, water, earth, and air, the four so-called elements. The search after the "philosopher's stone," which was to change base metal into silver and gold, and the universal "elixir," which was expected to cure all diseases and prolong life indefinitely, had, however, led the alchemists of the middle ages, partly or completely, to abandon the notion of four elements. For simple contemplation of natural objects they had substituted the practice of experiment, and, though during this long period the art of observation never grew to great perfection, enough was learned to show that other hypotheses were wanted to explain the facts discovered in the laboratory of the chemist. A new system of chemical principles was adopted, and all the various qualities of bodies were attributed to the three elements, or *tria prima*, *salt*, *sulphur*, and *mercury*, in various proportions, and incorporated in various ways.

Alchemists.

The phenomena of fire up to the end of the seventeenth century had been an impenetrable mystery. This was probably owing chiefly to the fact that the nature of common air was unknown, and the study of gases or "volatile spirits," as they had been called, had been almost entirely neglected. Experimenting with his air-pump Boyle found that a candle, charcoal, and sulphur would not burn in the receiver after removal of the air. Hooke, who had been assistant to Boyle at Oxford, also pointed out that air is necessary to combustion, and that it acts in virtue of an ingredient "like unto or the very same as that which is fixed in saltpetre." Mayow, in 1675, burned a candle under a bell glass and found the air so changed that a lighted candle would not burn in it; and Rey, a French physician, in 1680, discovered that metals, such as tin and lead, when calcined, increase in weight. From such observations the following important facts were therefore established:—Ordinary burning cannot take place without air; the same air cannot be used twice over; the use of bellows and the draught of a chimney show that, by increasing the supply of fresh air to a burning surface, the more rapid is the combustion; and lastly, that in burning there is no loss of substance, but that when air has free access there is a gain of weight.

BOYLE.

HOOKE.

MAYOW.

The great service, however, rendered to Chemistry by Robert Boyle consisted in showing that there was no sufficient evidence of the general existence of the alchemistic principles, salt, sulphur, and mercury, that the number of elements could not be limited, and in teaching the doctrine that things, such as gold, which cannot be decompounded, must, for the time, be regarded as simple. These are the elements of the modern chemist.

Fire, and the process of burning, have been from the earliest times subjects for wonder and curiosity, and even the object of worship. A theory which pretends to give an explanation of burning and of flame, and which connects, under a common explana-

tion, such phenomena with the changes which go on in the rusting of metals, the decay of organic matters, and the processes of putrefaction and fermentation, is deserving of careful attention. A comprehensive theory of this kind was the theory of "phlogiston," enunciated by Stahl (b. 1660, d. 1734). According to this doctrine, all combustible substances, as well as metals, owe their characteristic properties to the presence in them of a peculiar inflammable principle, *phlogiston*, together with a calx or ash. Substances like charcoal were supposed to be rich in phlogiston, while metals, such as iron, were supposed to contain little phlogiston, but much calx. The theory further taught that the phlogiston of one substance might be communicated to a calx, whereby it could become metallic or combustible, as when charcoal, heated with iron ore, makes iron, or, heated with litharge, it produces lead. The discovery that when a metal is roasted and converted into a calx it becomes heavier was sufficient to show that the theory was incorrect or incomplete, for it would be difficult to explain how the loss of something by a body could add to the weight of the body. Nevertheless, the doctrine was generally adopted, and all sorts of chemical changes were explained upon this hypothesis down to the time of Lavoisier, at the end of the eighteenth century.

STAHL and Phlogiston.

In the meantime, a long series of experimental researches were being carried on, with results of the highest importance to the science of Chemistry. In 1774, "dephlogisticated air" (oxygen), had been isolated from red precipitate of mercury by Priestley (b. 1733, d. 1804). The same process had already been used by Scheele (b. 1742, d. 1786), in Sweden, but not published till about two years later. Moreover, Scheele showed very clearly that the "fire-air," as he called it, obtained from this and other sources was really a constituent of common air, and that the latter owes its power as a supporter of combustion and of animal respiration to the presence of this ingredient. He seems to have understood the nature of common air, but was prevented from finding the true explanation of the process of burning in consequence of his persistent adherence to the theory of phlogiston. Priestley was also a phlogistian to the end of his life.

PRIESTLEY and SCHEELE.

Muriatic acid had been obtained from common salt a century and a half earlier by the alchemist Glauber. From this liquid a gas was produced by Scheele in 1774, which he called, in the language of the period, "dephlogisticated" muriatic acid. This gas, afterwards proved by Davy to be, like oxygen, a simple body or element, received from him the name *chlorine*, in allusion to its greenish colour. The inflammable air produced during the solution of the common metals iron and zinc in sulphuric acid had been noticed by Paracelsus in the sixteenth century, and had been examined by Boyle. But it was Cavendish (b. 1731, d. 1810) who showed, in 1784, that this air, united with the dephlogisticated air of Priestley, produced water, and nothing else. From this Cavendish drew the conclusion that "dephlogisticated air is only water deprived of phlogiston." The

CAVENDISH.

name *hydrogen*, or water-producer (from ὕδωρ, water, and γεννάω, to produce) was long afterwards given to this inflammable air in conformity with the system of nomenclature adopted by Lavoisier.

BLACK. In 1755, a paper entitled "Experiments on Magnesia Alba, Quicklime, and other Alkaline Substances," was published by Dr Black (b. 1728, d. 1799), then Professor of Chemistry in the University of Edinburgh, in which he showed that common magnesia "is a compound of a peculiar earth and fixed air," and that limestone and chalk consist of lime with the same fixed air, which can be driven out by a strong heat, as in the lime-kiln, and restored to the lime either by contact with alkalis, or on exposure to the air. The acrid character of quicklime and of caustic alkali is therefore not due, as had previously been supposed, to the addition of a peculiar acid, but to the removal of the fixed air, or, as it is now called, carbonic acid gas, or carbon dioxide. Such facts as these, and many others, formed the material out of which Lavoisier framed his new system of Chemistry.

LAVOISIER. The phlogistic theory had two defects: it assumed the existence of a principle supposed to be material, but whose existence was the creation of pure hypothesis, and it ignored the acknowledged influence of the air in combustion, and the increase of weight actually observed in the calcination of metals. Lavoisier (b. 1743, d. 1794) succeeded in giving the true interpretation to facts already long established. It was known that in the calcination of metals, and in the burning of sulphur and phosphorus in contact with air, there was not only an increase in the weight of the substance, due to the absorption of air, but that it was not the whole of the air, but one of its constituents, which thus became fixed in the solid compound. This constituent of air Lavoisier traced into the red calx of mercury, and, imitating the method of Priestley, he separated again the constituents of the calx by heating it, and thus obtained from it fluid quicksilver and the "vital" air. This, like the gas Priestley had called "dephlogisticated air," and like that which Scheele had called "fire-air," he found was specially active in combustion, and in supporting the respiration of animals. Insisting upon all these facts, Lavoisier showed that burning, rusting, and calcination are processes in which there is not a *decomposition* of the burning or rusting substance, as supposed by the phlogistic doctrine, but that there is a *combination* of the substance with the new air, the resulting compound being made up of the two united, without loss of any portion of either. This vital air he found also in fixed air from chalk, in phosphoric, sulphuric, sulphurous, nitric, and nitrous acids, and, recognising its connection with the production of acids, he gave to it the name "principe oxygine," since contracted into *oxygen* (from ὄξος, vinegar, and γεννάω, to produce), and called the compounds into which it was known to enter *oxides*.

Acids and *alkalis* form two of the most important classes of definite chemical compounds, and their chief qualities have been recognised from very early times. Acids are commonly sour to the

taste, soluble in water, and redden infusion of blue cabbage or litmus. Alkalis are more or less soluble in water. The solutions taste soapy, and they turn infusion of red cabbage or of violets green and litmus blue. Lavoisier showed that both these classes of compounds consist usually of oxides, and since it is commonly the property of alkalis to neutralise acids when mixed with them, the *salts* which result must also usually contain oxygen.

Muriatic acid, however, forms an important exception to Lavoisier's rule as to the composition of acids, for it contains no oxygen. The yellow gas obtained, as already stated, by Scheele was called by him dephlogisticated muriatic acid, a name which expressed the fact that it was muriatic acid deprived of its inflammable principle. Lavoisier regarded it as a compound of muriatic acid and oxygen, and it was not till 1810 that *chlorine*, as it was then called by Davy, was completely established among the elements. Davy mixed the dry gas with hydrogen, and showed that the two unite without contracting and without formation of water. Charcoal intensely ignited in the gas produced no oxide of carbon, and similarly potassium, sodium, tin, copper, phosphorus, and sulphur, when ignited in chlorine, produce compounds which have none of the properties of oxides. Other elements of similar characters have since been isolated,—iodine, by Courtois, in 1811; bromine, by Balard, in 1826; and fluorine, by Moissan, in 1886; and these are now recognised as forming, with chlorine, a natural group or family of elements possessing many chemical characters in common.

The composition of a compound may be expressed in reference solely to the elements of which it is composed, or the proportion of those elements may be stated. During the latter half of the eighteenth century attention had been given to experiments relating to the quantity of materials to be used or of products obtained in chemical processes, but it was not till after Lavoisier's time that the balance was commonly used in chemical investigations. Two German chemists, Wenzel and, later, Richter, had made a great many analyses of salts, and had made determinations of the amount of metallic oxide required to saturate several acids, but though they did in effect establish the important principle that in chemical changes definite weights of matter are concerned, it was not till the early years of the present century that the Law of Definite Proportions was so firmly established as to be generally recognised. Proust, a French chemist, proved that native carbonate of copper has the same composition as the carbonate prepared artificially by precipitation, and extending similar analytical inquiries to many oxides and sulphides, he provided a secure foundation for the doctrine that every chemical compound is definite in its nature, the ratio of the elements entering into its composition being fixed and invariable.

WENZEL and RICHTER.

PROUST.

From the days of Newton various attempts had been made to apply the doctrine of atoms to the explanation of the properties of matter, but owing to a lack of exact knowledge of the composition of

such familiar things as air and water, no practical shape had been given to the theory. But at about the time when Proust was labouring to establish the idea involved in the law of definite proportions just stated, further inquiries were being made by John Dalton (b. 1766, d. 1844) at Manchester. By what course of reasoning is not now known with certainty, he was led to adopt the view "that all bodies of sensible magnitude, whether liquid or solid, are constituted of a vast number of extremely small particles, or atoms of matter bound together by a force of attraction which is more or less powerful according to circumstances," and in his *New System of Chemical Philosophy*, published in 1808, he shows that this hypothesis is satisfactory but that hitherto no use had been made of it. The following passage sets forth very clearly Dalton's own application of his hypothesis:—"Chemical analysis and synthesis go no further than to the separation of particles one from another and to their reunion. No new creation or destruction of matter is within the reach of chemical agency. We might as well attempt to introduce a new planet into the solar system, or to annihilate one already in existence, as to create or destroy a particle of hydrogen. All the changes we can produce consist in separating particles that are in a state of cohesion or combination, and joining those that were previously at a distance" (*Chem. Phil.*, p. 212). In the course of his inquiries Dalton discovered the Law of Multiple Proportions. When two elements, A and B, unite together in more than one proportion, if we consider the quantities in which B unites with a fixed proportion, say one part by weight, of A, then these quantities bear a simple relation to each other. Thus, one part, by weight, of hydrogen combines with eight parts, by weight, of oxygen to form water, and with sixteen parts, by weight, of oxygen to form another compound called hydrogen peroxide: that is to say, in accordance with the law, the quantity of oxygen in the second compound is exactly twice the quantity of oxygen in the first, considered in relation to the same quantity of hydrogen in both. This would be an obvious deduction from the doctrine of atoms, for if one atom of hydrogen combines with oxygen, it must combine with either one atom or with two or more atoms of that element, a fraction of an atom * being by the hypothesis inadmissible. Dalton, however, did not limit himself to speculation, but made a large number of analyses with the object of determining the composition of bodies. Many of his experimental results were very inaccurate, and some of his assumptions were inconsistent with the conclusions derived from the more exact knowledge of modern times, but by turning to account the previously vague and useless doctrine concerning the particles of bodies, and bringing these notions into harmony with the facts of combination, he laid a foundation for the entire fabric of modern theoretical chemistry. Dalton's Atomic Theory is therefore entitled to rank with Lavoisier's antiphlogistic theory of combustion, as

DALTON.

* Something indivisible from α privative, and τέμνω, I cut. A group of united atoms forms a molecule. (*Moles*, Latin, a heap; *molecula*, diminutive.)

representing one of the most important steps that has ever been taken in the history of chemistry.

The establishment of the law of definite proportions had, however, not been accomplished without much controversy. A distinguished French chemist, Berthollet (b. 1748, d. 1822), maintained the view BER- that a substance tends to enter into combination not only in virtue THOLLET. of what has been called "affinity," but in proportion to its mass or quantity, and that the mutual action of two substances would be largely influenced by the physical properties of the resultant compounds, that is, their solubility, fusibility, or volatility; and he held that the composition of a compound was not necessarily definite and invariable, but was a matter of accident dependent upon the conditions under which it was formed. He seems to have believed that chemical attraction or affinity was a special manifestation of universal attraction, and not essentially different from adhesion and cohesion. Berthollet's views did not prevail in the controversy, for the law of definite proportions was finally placed beyond dispute by the work of Proust and other chemists. Nevertheless we now know how large an element of truth existed in the doctrine upheld by Berthollet, and have learnt to recognise its validity at the same time that fixity of composition of each chemical compound is an article in the belief of every chemist. The fact is that every chemical compound has a definite and invariable composition, but the extent to which a given chemical change may proceed is influenced by the relative masses of the acting bodies, as well as by the physical conditions of the experiment. This is too difficult a subject to be explained in an introductory chapter, but it will be referred to again when a sufficient number of facts and instances have been described.

The name of Sir Humphry Davy (b. 1778, d. 1829) is one of the DAVY. most famous in the early history of chemical science. Reference has already been made to his experiments upon chlorine, but his discovery of the metals sodium and potassium, derived from the alkalis, was an event of still greater importance. The substances called alkalis have been known from very early times. When the white ash obtained by burning wood or other vegetable matter is stirred up with water, a solution is obtained, after settlement of the insoluble matters, which possesses the property of cleansing, and was used for washing purposes long before the invention of soap. This solution, mixed with a vegetable dye, usually turns the reds and blues to a green colour; it also neutralises acids so that their sour taste and corrosive properties are lost. Further, it had long been known that when this solution is mixed with lime the "mild" alkali it contains is converted into "caustic" alkali [as already explained, *see* Black], which possesses the power of converting fat into soap. Lime is a substance of similar properties, but being far less soluble in water, it acts less vigorously than caustic potash. Up to the time of Davy, all attempts to decompose these substances had failed, and they were commonly regarded as simple or elementary bodies. The property of interacting with acids to form salts is common to sub-

stances such as red precipitate of mercury, litharge, or iron rust, and lime and the fixed alkalis. As the former had been shown by Lavoisier to consist of a metal united to oxygen, it might have been conjectured that lime and the alkalis potash and soda might have a like constitution, but the means of separating the constituents remained unknown. The Voltaic battery had been invented at the end of the eighteenth century, and had been used for the decomposition of water and of various salts in solution. Davy, turning this knowledge to account, succeeded, with the aid of a powerful battery of zinc and copper plates, in producing a current strong enough to decompose potash and soda, in 1807, and in showing that both these substances contain a metal. Lime, baryta, and magnesia were also shown to contain a metallic basis. The properties of the new metals sodium and potassium were found to be very remarkable. They attack even cold water violently, reproducing the caustic alkali, and liberating hydrogen in the form of gas. The action of potassium is so strong that it causes the ignition of the escaping hydrogen, and thus appears itself to burst into flame. These metals also differ from all metals known at that time in their remarkably low specific gravities, being so light as to float on water. The energy with which both these elements unite with oxygen and with chlorine suggests their use for the liberation of other elements from their compounds, and, in fact, several elements, such as borax, silicon, aluminium, and magnesium, were first obtained in the pure state by heating the chlorides with metallic potassium or sodium.

In all the earlier days of chemical investigation the manipulation of gases had offered considerable difficulties, and almost down to Robert Boyle's time the "volatile spirits" had occupied but little attention, but when the means of collecting air and other gases in jars filled with water began to be practised, the different kinds of air received more notice. Priestley's discoveries especially, and his systematic use of the water trough and the mercurial trough for collecting air, gave encouragement to this branch of chemical inquiry.

Dalton devoted some years to the study of atmospheric air, and to various gaseous compounds, such as the oxides of nitrogen and the gas from ponds (marsh gas), and olefiant gas. It is therefore remarkable that, when the important announcement was made that gases in combining together unite in volumes which have a simple numerical relation among themselves, he should have been unwilling to admit the truth of it. This observation was made by a famous French chemist, Gay-Lussac (b. 1778, d. 1850), twelve years younger than Dalton, and the contemporary of Davy. In a memoir published in 1808, Gay-Lussac gave an account of his experiments upon the combination of gases together, and the conclusions drawn from them. A quarter of a century earlier Cavendish had shown that oxygen unites with hydrogen in the proportion of one measure of the former to two measures of the latter. Gay-Lussac and Humbolt had repeated this experiment with the same result, and Gay-Lussac

GAY-LUSSAC.

showed that ammonia combines with an equal volume of hydrogen chloride (muriatic acid), and with half its volume of carbonic acid gas, and, by referring to the analysis of various gases by other chemists, he was able to show that gases combine in simple proportions by measure, such as 1 to 1, 1 to 2, 1 to 3, as in the following examples :—

Ammonia is composed of	nitrogen 100	to hydrogen 300	volumes.
Nitrous oxide is composed of	nitrogen 100	to oxygen 50	volumes.
Nitric oxide ,, ,,	nitrogen 100	to oxygen 100	,,
Nitric peroxide contains	nitrogen 100	to oxygen 200	,,

It is obvious that the discovery of such relations as these really served to consolidate the basis of the atomic theory, and ought to have been more readily acknowledged than they were by Dalton. Another conception was, however, needed to render clear the significance of these facts. This was supplied in a memoir published by an Italian physicist, Avogadro, in 1811. He there enunciates the important hypothesis that "the number of integral molecules in any gases is always the same for equal volumes, or always proportional to the volumes." This has now been confirmed abundantly by all subsequent experience, and hence is generally adopted as one of the fundamental doctrines of Chemistry. The consequences of the application of this doctrine will be explained more in detail at a later stage. If this statement is true, it is obvious that there must be a direct relation between the densities of gases and the relative masses of the molecules of which they are composed. AVOGADRO.

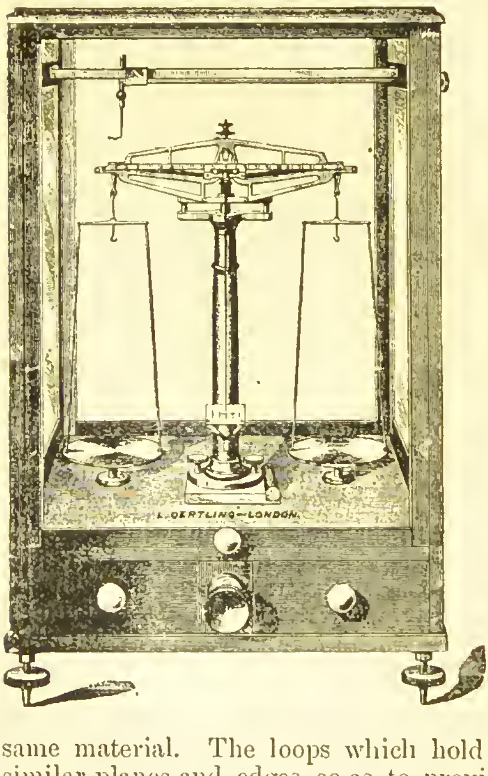
It is now time to refer to the work of the great Swedish chemist Berzelius (b. 1779, d. 1848), by whose labours the doctrine of definite proportions and the atomic theory of Dalton were completed and consolidated. Berzelius devoted many years to the experimental determination of the combining proportions, often improperly referred to as the atomic weights, of the more important elements, and the numbers calculated from his results are so near to the true values that, in most cases, more modern investigations have led to only slight alterations. That they were far more accurate than the numbers given by Dalton will be perceived from a comparison of a few cases, such as the following :— BERZELIUS.

Name of Element.	Combining weights according to Dalton.	Berzelius.	Modern Researches.
Nitrogen.	5	4·66	4·68 (Stas).
Oxygen.	7	8·0	7·98 (Dumas).
Sulphur.	13	16·06	16·03 (Stas).
Lead.	95	103·57	103·45 (Stas).

As already stated, it was not till towards the end of the eighteenth century that the weights of substances employed or obtained in the course of chemical experiments were systematically estimated, and the foundations of quantitative analysis were laid. The experiments of Black on magnesia and lime (p. 4), many of the investigations of

Lavoisier, and a large part of the work of Dalton involved the employment of scales and weights. So also did the investigation of the composition of salts by Wenzel and Richter and by Proust, and the analysis of minerals, which had made much progress, especially in the hands of a German chemist, Klaproth. But the scales employed up to this time by the chemist had been usually the comparatively rough instruments used by the apothecary for weighing out medicines. The most exact operations of weighing had been, of course, those forming part of the process of assaying the precious metals gold and silver. When the importance of the utmost possible accuracy in chemical analysis became apparent, as in the determination of combining weights, the balances used in chemical laboratories began to be greatly improved. The theory of the common balance is very simple. It consists of a bar or lever supported in the centre, and having at each end a pan, the one for the substance to be weighed, the other for the weights. It would be unprofitable to attempt to trace the various improvements which have been gradually introduced in the construction of the instrument for scientific purposes: we must be content with describing a modern balance, such as is now commonly employed, and which is shown in figure 1. The beam is usually of brass, and is supported centrally by a steel, or better, an agate, edge, which rests upon a polished plane of the same material. The loops which hold the pans are suspended by similar planes and edges, so as to provide the most perfect possible freedom of movement, in order that the pans may always hang vertically. To avoid injury to the steel or agate edges, the beam rests, when the balance is not in use, upon two supports, and the edges from which the pans depend are, at the same time, lifted from their planes. The movements of the beam are indicated by a fine steel index, which is attached to its middle point and moves to and fro across a divided ivory scale. The instrument is enclosed in a glass case, not only to preserve it from dust and fumes, but to avoid

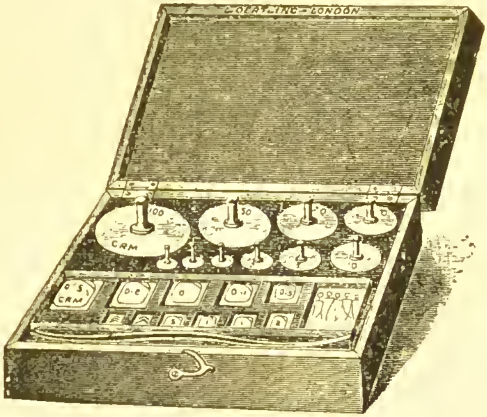
Fig. 1.



the influence of currents of air, which would interfere seriously with its indications.

Theoretically it is a matter of no importance what system of weights is employed, provided each weight bears a definite and known relation to the others; but as the result of experience, chemists generally have been led to adopt the weights of the French metric system, the divisions of which are decimal fractions of the unit weight. (*See* Appendix Tables IV. and V.) The weights used in analytical work are made, the larger, of polished and gilded brass, the smaller, of aluminium or platinum, and are enclosed in a box to preserve them from injury. Such weights usually range from 50 grams down to 1 centigram or ·01 gram. One-tenth or one-hundredth of this weight is usually estimated, not by a weight placed in the pan, but, more conveniently, by means of a "rider" of gold wire weighing 1 centigram, which can be deposited upon the beam at any of the divisions marked upon it. Figure 2 shows a box of weights of the usual form.

Fig. 2.



Berzelius did not confine his attention to analytical work. He had theories concerning the cause of chemical combination which were for some years generally adopted by the chemical world, but ultimately were overthrown, and have only been revived in recent times in a considerably modified form. It would be unprofitable to attempt at this stage the discussion of theories concerning chemical attraction, but we must remember that Chemistry is indebted to Berzelius for another proposal which has been of great service in the development of theoretical Chemistry. Berzelius introduced the system of symbols, which, since his time, has been almost universally employed by chemists. The alchemists employed fantastic symbols which were apparently designed to supply mystery rather than clearness. Dalton had represented his atoms by symbols which consisted of circles having arbitrary marks upon them, to distinguish one kind from another. These, however, would be troublesome to write, and do not explain themselves like the symbols of Berzelius, which consist of the initial capital letter of the name of the element. Thus, H represents hydrogen, O oxygen, S sulphur, C carbon, Pb (plumbum) lead, etc., and these being adopted to represent *one atom* of the element, the composition of a compound can be easily expressed by writing two symbols side

by side, adding, as may be necessary, a co-efficient to indicate the number of atoms of each element. To express hydrogen chloride, for example, a compound of hydrogen and chlorine, the formula HCl is used ; to express water H_2O, ammonia NH_3, sulphuric acid, H_2SO_4, etc. This matter will be explained in more detail a little later (*see* p. 16). Since the days of Berzelius, of Dalton, Davy, and Gay-Lussac, a host of workers has arisen, among the most notable of whom should be mentioned Liebig and Wöhler, in Germany, Dumas, Laurent, and Gerhardt, in France, Faraday and Graham, in England, beside many others, who, like them, have now passed away. The science of Chemistry has made immense advances, and its boundaries have become so wide that the entire subject is beyond the capacity of any one human mind, while it becomes more and more difficult to determine exactly the limits which divide chemical phenomena from those which are, perhaps, only mechanical or physical.

The science of Chemistry has still for its primary object the study of the materials which enter into the composition of the earth, the sea, and the air, and of the various organised and living beings which inhabit them, but it is no longer sufficient to determine composition. The aim of the chemist is to ascertain the relation of composition to the physical properties of a body, and the study of "isomerism" has led to still greater developments. It was discovered about 1820 that the same elements united in the same proportions do not necessarily give rise to the same compound. Bodies having the same composition, but different properties, are called *isomeric*, and the study of isomeric compounds has contributed largely to substantiate the view, derived originally from other facts and considerations, that it is possible to represent, not merely the nature and the number of the atoms entering into a molecule, but the order in which these atoms are united together, and even to conjecture, with some show of probability, the geometrical arrangement in space of the particles thus united. The study of this department of the science is called "Stereo-chemistry," but this, and many other theoretical aspects of the subject must be postponed till the student has become acquainted, not only with the properties of the chief elements, but with the origin, properties, and metamorphoses of those very numerous compounds of carbon which are usually considered together under the title "Organic Chemistry," a subject which, on account of its extent and complexity, is necessarily dealt with in separate works.

We must now proceed to a few general statements and explanations which will be found useful in the chapters following, in which the sources and properties of the non-metallic elements, and of their chief compounds, are described.

The elementary bodies, at present recognised, are upwards of seventy in number, and about fifty of them belong to the class of *metals*. Several of them are of recent discovery, and many are as yet very imperfectly known. The distinction between metals and

Table of Elements with their Symbols and Atomic Weights.

Name.	Symbol.	Atomic Weight.
ALUMINIUM	Al	27
Antimony (Stibium)	Sb	120
Argon*	A	40
Arsenic	As	75
Barium	Ba	137
Beryllium	Be	9·1
Bismuth	Bi	208
Boron*	B	11
BROMINE*	Br	80
Cadmium	Cd	112
Cæsium	Cs	133
CALCIUM	Ca	40
CARBON*	C	12
Cerium	Ce	140
CHLORINE*	Cl	35·4
Chromium	Cr	52
Cobalt	Co	59
COPPER (Cuprum)	Cu	63
Decipium	Dp	?
Didymium	D	141
Dysprosium	Dy	?
Erbium	E	166
FLUORINE*	F	19
Gadolinium	Gd	156
Gallium	Ga	70
Germanium	Ge	72
Gold (Aurum)	Au	197
Helium*	He	4
Holmium	Ho	?
HYDROGEN*	H	1
Indium	In	113
IODINE*	I	127
Iridium	Ir	193
IRON (Ferrum)	Fe	56
Lanthanum	La	138
LEAD (Plumbum)	Pb	207
Lithium	Li	7
Magnesium	Mg	24
MANGANESE	Mn	55
MERCURY (Hydrargyrum)	Hg	200
Molybdenum	Mo	96
Nickel	Ni	58
Niobium	Nb	94
NITROGEN*	N	14
Osmium	Os	190
OXYGEN*	O	16
Palladium	Pd	106
PHOSPHORUS*	P	31
PLATINUM	Pt	194·3
POTASSIUM (Kalium)	K	39
Praseodymium	Pr	144
Rhodium	Rh	103
Rubidium	Rb	85
Ruthenium	Ru	101·4
Samarium	Sm	150
Scandium	Sc	44
Selenion*	Se	79
SILICON*	Si	28
SILVER (Argentum)	Ag	107·6
SODIUM (Natrium)	Na	23
Strontium	Sr	87·3
SULPHUR*	S	32
Tantalum	Ta	182
Tellurium	Te	126 ?
Terbium	Tb	148 ?
Thallium	Tl	204
Thorium	Th	232
Thulium	Tm	171 ?
TIN (Stannum)	Sn	117·3
Titanium	Ti	48
Tungsten (Wolfram)	W	184
Uranium	U	240
Vanadium	V	51·1
Ytterbium	Yb	173 ?
Yttrium	Y	90
ZINC	Zn	65
Zirconium	Zr	90

non-metallic substances, although very convenient for purposes of description, is entirely arbitrary, the two classes not being separated by any exact line of demarcation.

The names of the elements are given in the foregoing table. Opposite to them in the third column are placed certain numbers, which express the proportions in which they combine together, or simple multiples of those proportions; these numbers, as already explained, are called A t o m i c W e i g h t s. In the second column are placed symbols by which these relative weights are denoted; these symbols are formed of the first letters of the Latin names of the elements, a second letter being added when the names of two or more elements begin with the same letter.

The names of the most important elements are distinguished by the largest and most conspicuous type; those next in importance, by small capitals; while the names of elements which are of rare occurrence, or of which our knowledge is still imperfect, are printed in ordinary type. The names with an asterisk are those of Non-metallic Elements, the others are names of Metals or Metalloids.

It must be distinctly understood that the atomic or combining weights assigned to the elements are merely relative. The number 1 assigned to hydrogen may be taken to represent a grain, ounce, pound, gram, kilogram, etc., and the numbers assigned to the other elements will then represent so many grains, ounces, pounds, grams, kilograms, etc. Hydrogen is taken as the unit of the scale, because its combining weight is smaller than that of any other element; but this is merely a matter of convenience; in the older tables of atomic weights that of oxygen was assumed as 100, that of carbon being then 75, that of hydrogen 6·25, etc., etc. The methods by which atomic weights are determined will be explained in detail after the non-metallic elements and their compounds have been described.

By the combination of the elements in various proportions, and in groups of two, three, or more together, all compound bodies are produced. And here it is important to state clearly the characters which distinguish definite chemical combination from mechanical mixture, and from that kind of adhesion which gives rise to the solution of a solid in a liquid. Bodies may be mixed together in any proportion whatever, the mixture always exhibiting properties intermediate between those of its constituents, and in regular gradation, according to the quantity of each that may be present, as may be seen in the fusion together of metals to form alloys, in the mixture of water with alcohol, of alcohol with ether, and of different oils one with the other. A solid body may also be dissolved in a liquid—salt or sugar in water, for example—in any proportion up to a certain limit, the solution likewise exhibiting a regular gradation of physical properties, according to the quantity of the solid taken up. But a true chemical compound exhibits properties totally different from those of either of its constituent elements, and the proportion of these constituents which form that particular

compound admits of no variation whatever. Water, for example, is composed of two elements, oxygen and hydrogen, which, when separated from one another, appear as colourless gases, differing widely in their properties one from the other, and from water in the state of vapour; moreover, water, whether obtained from natural sources, or formed by direct combination of its elements, always contains in 100 parts by weight, 88·9 parts of oxygen and 11·1 of hydrogen. Common salt, to take another example, is a compound of chlorine and sodium, the former of which, in the separate state, is a yellowish-green gas, the latter a yellowish-white highly lustrous metal, capable of burning in the air, and decomposing water; moreover, from whatever part of the world, and by whatever process, the salt may be obtained, 100 parts of it invariably contain 39·6 parts of sodium and 60·4 parts of chlorine. Further, when two or more compounds are formed of the same elements, there is no gradual blending of one into the other, as in the case of mixtures, but each compound is sharply defined, exhibiting properties distinct from those of the others, and of the elements themselves in the separate state. Thus, there are two compounds of carbon and oxygen, one of which, containing 3 parts by weight of carbon with 4 of oxygen, is an inflammable gas, lighter than atmospheric air, and not absorbed by cold solution of potash; while the other, which contains 3 parts of carbon and 8 of oxygen, is non-inflammable, heavier than air, and is easily absorbed by potash.

Distribution of the Chief Elements.

Oxygen is the most widely diffused of all the elementary bodies. It is under ordinary circumstances a gas, and, mixed with nitrogen, constitutes the air which we breathe. In combination with hydrogen it forms water. In the pure state it is a colourless inodorous gas, in which inflammable bodies, such as wood, oil, sulphur, etc., burn much more rapidly than in common air.

Nitrogen, the other chief constituent of the air, is also a colourless gas, non-inflammable, and differing from oxygen in not being capable of maintaining the combustion of other bodies, so that a lighted taper immersed in it is immediately extinguished.

Hydrogen, the other constituent of water, is in the free state also a gas, and is the lightest of all known bodies. In presence of oxygen or common air, it is very inflammable, and burns with a pale blue flame, producing water.

Carbon is a constituent of all vegetable and animal substances, existing therein in combination either with hydrogen alone, or with hydrogen and oxygen, or with hydrogen, oxygen, and nitrogen. When separated from these elements, it is for the most part a black solid body, well known under the names of charcoal, coke, lamp-black, and plumbago, or black-lead. It occurs also naturally in the pure state, forming transparent crystals known as diamond.

Chlorine, Bromine, and Iodine exist in sea-water (hence

called *Halogen-elements*, from ἅλς, the sea), in combination chiefly with sodium. Chlorine in the free state is a yellowish-green gas, bromine a red liquid, iodine a greyish-black crystalline solid. Of these elements, chlorine is by far the most abundant, its compound with sodium forming common sea-salt. Fluorine is an element closely allied in its chemical relations to the three last mentioned. In combination with calcium it constitutes the crystallised mineral called fluorspar.

Sulphur, a well-known substance, occurs as a yellow crystalline solid in volcanic districts, and abundantly in various parts of the world in combination with iron, copper, lead, and other metals, forming compounds called *sulphides*. Selenion and Tellurium are rare elements, allied to sulphur, and likewise found in combination with metals.

Phosphorus, is a highly inflammable solid body, which burns rapidly in contact with the air, being converted, by combination with oxygen, into *phosphoric oxide*, a compound which, in combination with lime, occurs very abundantly in nature, forming the minerals called phosphorite and apatite, and is the chief mineral constituent of the bones of animals. Arsenic, sometimes regarded as a metal, is an element closely allied in its chemical relations to phosphorus, and occurring in nature in combination with oxygen, sulphur, and various metals.

Silicon is a very abundant and important element, not occurring in nature in the free state, but forming, in combination with oxygen, the oxide called *silica*, which in the form of quartz, flint, and sandstone, and as a constituent of granite, gneiss, and other ancient rocks, forms a very large portion of the crust of the earth. Boron, an element analogous in many of its properties to silicon, occurs naturally in combination with oxygen, forming boric or boracic acid, which is a constituent of several minerals, and occurs somewhat abundantly in solution in certain natural waters.

Of the fifty-four metals, seven only were known in ancient times, viz., iron, copper, lead, tin, mercury, silver, and gold; of these, by far the most abundant and important is iron. Of the metals more recently discovered, the most abundant are sodium, potassium, calcium, and aluminium. Sodium, as already observed, forms, in combination with chlorine, the chief saline constituent of sea-water. Potassium, which resembles it in many respects, exists also in the sea, and is a constituent of all plants. Calcium is the metallic constituent of limestone, and aluminium of clay.

Chemical Nomenclature and Notation.—The names of the elements exhibit considerable diversity in consequence of the retention of names which were in use before the end of the last century, when for the first time the nature of the several classes of elementary substances began to be recognised. Thus we have the words iron, copper, lead, tin, silver, and gold which are of more or less ancient origin, while bismuth, zinc, cobalt, and nickel are

derived from more modern German words. The only uniformity of usage which has generally been adopted is the practice of using the terminal syllable *-ium* in framing the names of metals discovered within the present century. Potassium was the name given by Davy to the metallic basis of potash and sodium to that of soda, while aluminium, magnesium, barium, strontium, calcium, indium, thallium, etc., are words which have in like manner been adopted with the view of indicating the metallic character of these and similar elements.

The names of compounds exhibit greater uniformity and are constructed in accordance with well recognised rules. When two elements unite together to form a compound the name of the metallic or electropositive element is usually written first and is followed by the name of the non-metallic component having its final syllable changed into *-ide*. Thus a compound of oxygen is called an *oxide*, of chlorine a *chloride*, of sulphur with hydrogen or metal a *sulphide* and so forth. The systematic name of lime for example would be calcium oxide, of common salt, sodium chloride. The symbols used to represent atomic proportions of the elements are employed in a like order, so that lime would be expressed by the formula CaO, and common salt by the formula $NaCl$.

When two elements unite together in several proportions, according to the law of multiples (p. 6) a system of latin, or more usually greek numeral prefixes is employed to indicate the composition, and these correspond to the figures which are used in the formula. The following examples serve sufficiently to explain the use of both name and formula.

Oxides of Barium.

Name.	Formula.	Composition.		
		Barium.		Oxygen.
Barium monoxide, . .	BaO,	137	+	16
Barium dioxide, . . .	BaO_2,	137	+	32

Sulphides of Potassium.

Name.	Formula.	Composition.		
		Potassium.		Sulphur.
Potassium monosulphide, .	$K_2\cancel{O}$,S	78	+	32
Potassium disulphide, .	K_2S_2,	78	+	64
Potassium trisulphide, .	K_2S_3,	78	+	96
Potassium tetrasulphide, .	K_2S_4,	78	+	128
Potassium pentasulphide, .	K_2S_5,	78	+	160

It sometimes happens that the number of atoms is not known, or for various reasons it is undesirable to attempt to express the number in this fashion in the name. In that case it is preferable to indicate by the termination the relative proportions of the negative element, always reserving the syllable *-ic* for the compound which

contains the larger proportion of this element, and the syllable *-ous* for that which contains the smaller proportion. Thus,

Oxides of Nitrogen.

Name.	Formula.	Composition. Nitrogen.		Oxygen.
Nitrous oxide . . .	N_2O,	28	+	16
Nitric oxide . . .	NO,	14	+	16

Chlorides of Iron.

Name.	Formula.	Composition. Iron.		Chlorine.
Ferrous chloride, . .	$FeCl_2$,	56	+	70·8
Ferric chloride, . . .	$FeCl_3$,	56	+	106·2

The acids or hydrogen salts are distinguished by a similar nomenclature. Thus we have two acids containing hydrogen, sulphur, and oxygen, which are distinguished by the names sulphurous and sulphuric acids, of which the latter contains the larger proportion of oxygen. In this and other series, however, it often happens that there are other compounds which contain either a larger or a smaller proportion of oxygen than the two most important terms, and these it is customary to distinguish by the prefixes *hypo* and *per* (greek ὑπό under, per from ὑπὲρ over). The following series will sufficiently explain the application of this system.

Name.	Formula.	Composition. Hydrogen.	Chlorine.	Oxygen.
Hypochlorous acid, .	$HClO$,	1	35·4	16
Chlorous acid, . .	$HClO_2$,	1	35·4	32
Chloric acid, . .	$HClO_3$,	1	35·4	48
Perchloric acid, .	$HClO_4$,	1	35·4	64

The salts formed by the replacement of the hydrogen in the acid by a metal would receive similar names, the termination *-ic* being exchanged for *-ate* and the syllable *-ous* for *-ite* as in the following example, which exhibits the names of the potassium salts derived from the foregoing series of acids.

Name.	Formula.	Composition. Potassium.	Chlorine.	Oxygen.
Potassium hypochlorite,	$KClO$,	39	35·4	16
Potassium chlorite,	$KClO_2$,	39	35·4	32
Potassium chlorate,	$KClO_3$,	39	35·4	48
Potassium perchlorate,	$KClO_4$,	39	35·4	64

The multiplication of a group of dissimilar atoms is denoted by placing a numeral to the left of the group of symbols, thus, $3HCl$ denotes 3 molecules of hydrogen chloride ; $2H_2SO_4$ stands for 2 molecules of hydrogen sulphate.

The combination of two groups or molecules is indicated by placing their symbols in juxtaposition, with a point between them : thus $ZnO.SO_3$ denotes a compound of zinc oxide with sulphur trioxide ;

$K_2O.H_2O$, a compound of potassium oxide with hydrogen oxide or water. Sometimes the sign + is used instead of the point, but the sign of addition is best and more commonly employed to signify *mixture* of two substances rather than chemical combination between them. To express the multiplication of such a group, the whole is enclosed in brackets, and a numeral placed on the left; *e.g.*, $2(ZnO.SO_3)$; $3(K_2O.H_2O)$, etc. If the brackets were omitted, the numeral would affect only the symbols to the left of the point; thus $3K_2O.H_2O$ signifies 3 potassium oxide and 1 water, not 3 potassium oxide and 3 water. The neglect of this distinction often leads to considerable confusion in chemical notation.

Chemical Equations.—The greater number of chemical changes consist either in the direct addition or separation of elements, or in exchange of elements between interacting bodies, the latter being by far the most frequent form of chemical change.

Chemical reactions may be represented symbolically in the form of equations, the symbols of the reacting substances being placed on the left hand, and those of the new substances resulting from the change, on the right: for example—

1. Resolution of mercuric oxide by heat into mercury and oxygen—

$$2HgO = 2Hg + O_2.$$

2. Resolution of manganese dioxide by heat into manganoso-manganic oxide and oxygen—

$$3MnO_2 = Mn_3O_4 + O_2.$$

3. Action of zinc on hydrogen chloride, producing zinc chloride and free hydrogen—

$$2HCl + Zn = ZnCl_2 + H_2.$$

4. Action of zinc oxide on hydrogen chloride or hydrogen sulphate, producing zinc chloride or zinc sulphate and water—

$$2HCl + ZnO = ZnCl_2 + H_2O,$$

and

$$H_2SO_4 + ZnO = ZnSO_4 + H_2O.$$

5. Action of sodium carbonate on calcium chloride producing sodium chloride and calcium carbonate—

$$Na_2CO_3 + CaCl_2 = 2NaCl + CaCO_3.$$

It need scarcely be observed that the test of correctness of such an equation is, that the number of atoms of each element on one side should be equal to the number of atoms of the same element on the other side.

Any such symbolical equation may be converted into a numerical equation, by substituting for each of the chemical symbols its numerical value from the table of atomic weights. Thus, in the last

equation Na_2CO_3 stands for $23 \times 2 + 12 + 16 \times 3$, or 106 parts by weight of sodium carbonate; while $CaCl_2$ represents $40 + 35{\cdot}4 \times 2$, or 110·8 parts by weight of calcium chloride: these, by their interaction, produce $(23 + 35{\cdot}4) \times 2$, or 116·8 parts of sodium chloride, and $40 + 12 + 16 \times 3$, or 100 parts of calcium carbonate. Thus, $106 + 110{\cdot}8$ parts of materials yield $116{\cdot}8 + 100$ parts by weight of products, that is, an equal weight.

The laws of chemical action and their expression by symbols and equations will receive abundant illustration in the special descriptions which follow; their general consideration will also be more fully developed in a subsequent part of the work.

CHEMISTRY OF THE NON-METALLIC ELEMENTS.

HYDROGEN.

Symbol, H. Atomic weight, 1. Density, 1.

Hydrogen is known in the uncombined state as a colourless inflammable gas existing among the emanations of volcanoes and pent up under pressure in minute cavities distributed generally throughout granite, gneiss, and many crystalline rocks belonging to the oldest geological formations, as well as more recent volcanic rocks. There is also little doubt that hydrogen exists in large quantity in the sun and in many stars. On the earth it chiefly exists in the form of its oxide, water.*

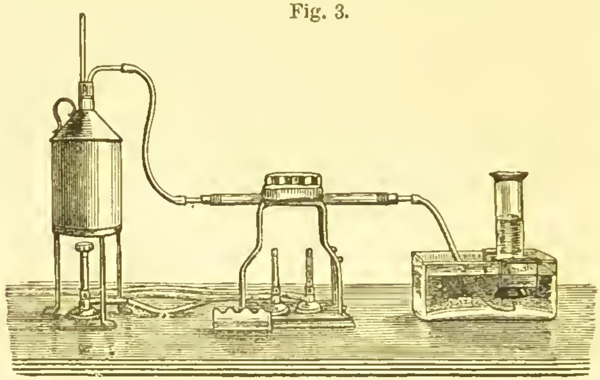
Experiment.—Take a piece of iron gas pipe, 1 inch in diameter and about 1 foot long, which has been cut off smoothly at each end. Fit into each extremity a cork, through which passes air-tight a short piece of glass tubing.† Now introduce into the iron tube a quantity of small nails, so that they may occupy about 4 inches in the middle of the tube. Support the tube at each end, so that by means of two large Bunsen burners the part containing the nails may be heated to redness. When the tube is as hot as possible, attach one extremity to a tube leading from a flask or tin can containing water kept boiling, so that a current of steam may be made to traverse the heated nails. The connection is best made by a piece of rubber tubing, and by a short length of the same material the steam which issues from the further extremity of the tube may be conveyed into a basin of water. It will then be found that the whole of the steam is not condensed ; bubbles of gas rise and escape. If now a test-tube or small jar is filled with water and inverted over the escape-tube, the gas will rise into the jar and gradually displace the water. The gas is hydrogen. On lifting the jar when filled with gas and applying a flame, the gas takes fire and burns with a scarcely visible light. The nails will be found to be encrusted with a dark coloured oxide of iron, the

* Hence the name, from ὕδωρ, water, and γεν, a root signifying production.

† A little practice will soon enable the student to construct and arrange a variety of useful forms of apparatus. Glass tube may be cut by scratching with a file, and then applying a little force with both hands. It may be softened and bent, when of small dimensions, by the flame of a spirit-lamp, or by a gas jet. Corks may be perforated by a heated wire, and the hole rendered smooth and cylindrical by a round file ; or a cork-borer may be used. Complete instructions for glass working may be found in Shenstone's "Glass-Blowing."

composition of which is expressed by the formula Fe_3O_4. The following figure shows the disposition of the apparatus :—

Fig. 3.



Hydrogen is, however, more easily obtained by decomposing hydrochloric or dilute sulphuric acid with zinc, the metal then displacing the hydrogen and forming a compound with the elements previously united with the hydrogen. Thus when hydrochloric acid is used, 32·5 parts of zinc are dissolved for every 1 part by weight of hydrogen obtained, or 1 atom of zinc (atomic weight, 65) takes the place of 2 atoms of hydrogen (atomic weight, 1), and by combining with the chlorine, produces a molecule of zinc chloride. This is shown by the equation already given (page 19).

Zinc has no action upon sulphuric acid unless heated or diluted with water. In the former case a somewhat complicated action occurs, and no hydrogen is obtained. In the latter case the action may be expressed by the following equation :—

$$H_2SO_4.H_2O + Zn = ZnSO_4.H_2O + H_2$$

or

$$H_4SO_5 + Zn = ZnH_2SO_5 + H_2.$$

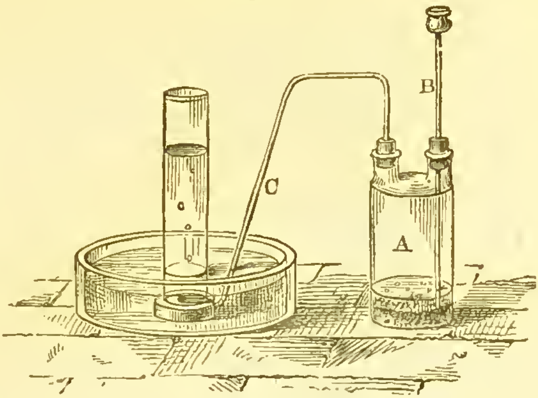
The simplest method of preparing the gas is the following :—

Experiment.—A two-necked bottle is fitted with sound corks perforated by holes for the reception of a small tube-funnel reaching nearly to the bottom of the bottle, and a piece of bent glass tube to convey away the disengaged gas (as shown in figure 4). Granulated zinc, or scraps of the sheet metal, are put into the bottle, together with a little water, and sulphuric acid slowly added by the funnel, the point of which should dip into the liquid. The evolution of gas is easily regulated by the supply of acid ; and when enough has been discharged to expel the air of the vessel, it may be collected over water in a jar, or passed into a gas-holder. In the absence of zinc, filings of iron or small nails may be used, but with less advantage.

Hydrogen is colourless, tasteless, and inodorous when quite pure. To obtain it in this condition, it must be prepared from the purest

zinc* that can be obtained, and passed in succession through solutions of potash and silver nitrate. When prepared from commercial zinc, it has a slight smell, due to impurity, and when iron has been used, the odour is very strong and disagreeable. It is inflammable, and burns, when kindled, with a pale bluish flame, evolving much heat, but very little light. The product of the combustion is water.

Fig. 4.



Experiment.—Having collected a jar full of hydrogen, lift it from the water, keeping the mouth downwards. Now push up into the gas a lighted taper. The flame of the taper will be put out, but the gas will burn at the mouth where it meets the air.

Experiment.—Fill a wide-mouthed bottle or jar with water, invert it in the trough and allow hydrogen to enter till somewhat less than one-third of the water has been displaced. Then lift the jar so that air takes the place of the remaining water. Close the jar with a glass plate and shake it up and down once or twice. Then remove the plate and instantly apply a flame. A sharp explosion follows. From this experiment we learn that it is dangerous to apply a light to the escape tube of the generating apparatus till time has been allowed for the hydrogen to drive out the whole of the air, inasmuch as the explosion which would certainly follow might be sufficiently powerful to burst the bottle.

Experiment.—It may now be supposed that since several jars of hydrogen have been collected and tested, the air has been completely expelled from the apparatus. Remove the delivery tube from which the gas escapes into the water and substitute for it a small U-shaped drying tube containing some broken glass or pumice-stone wetted with strong sulphuric acid. This substance absorbs moisture very quickly, and if the hydrogen is now allowed to pass through this tube, the water vapour which it brings with it will be retained by the sulphuric acid, and the gas will escape from the extremity quite dry.

If the issuing jet of gas is ignited, it will burn with a hot but scarcely visible flame. A cold glass held over it becomes covered with dew, and if a flask filled with cold water be suspended a few

* When very pure zinc is used, the action of the acid is very slow. If this is found to be the case, the addition of a few drops of solution of copper sulphate or of platinic chloride to the contents of the bottle will promote the action without affecting the purity of the gas.

inches above the flame, it will speedily collect upon the outside drops of water formed by the combination of the burning hydrogen with the oxygen of the air.

Hydrogen is the lightest substance known, its density being ·0693, referred to that of air as unity. The weight of a litre of hydrogen at 0° C., and under a barometric pressure of 0·760 metre, is 0·0896 gram; consequently a gram of hydrogen occupies a space of 11·16 litres.* At 60° F., and 30 inches barometric pressure, 100 cubic inches weigh 2·14 grains. Its coefficient of solubility in water is ·019.

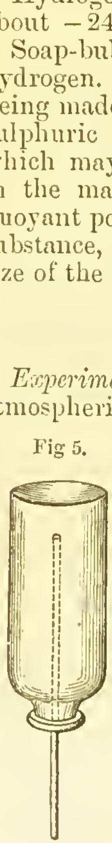
Hydrogen is liquefiable by cold and pressure; the liquid boils at about −243°, under atmospheric pressure.

Soap-bubbles and small collodion balloons ascend when filled with hydrogen. Hydrogen was formerly used also for filling air-balloons, being made for the purpose on the spot from zinc or iron and dilute sulphuric acid; but its use is now superseded by that of coal gas, which may be made very light by employing a high temperature in the manufacture. Although far inferior to pure hydrogen in buoyant power, it is found in practice to possess advantages over that substance, while its greater density is compensated by increasing the size of the balloon.

Collection and Preservation of Gases.

Experiment.—When a gas is much lighter or much heavier than atmospheric air, it may often be collected and examined without the aid of the water trough. A bottle or narrow jar may be filled with hydrogen without much admixture of air, by inverting it over the extremity of an upright tube delivering the gas. In a short time, if the supply be copious, the air will be wholly displaced, and the vessel filled. It may now be removed, the vertical position being carefully retained, and closed by a stopper or a glass plate. If the mouth of the jar be wide, it must be partially closed by a piece of card-board during the operation. This method of collecting gases by displacement is often extremely useful.

Fig 5.



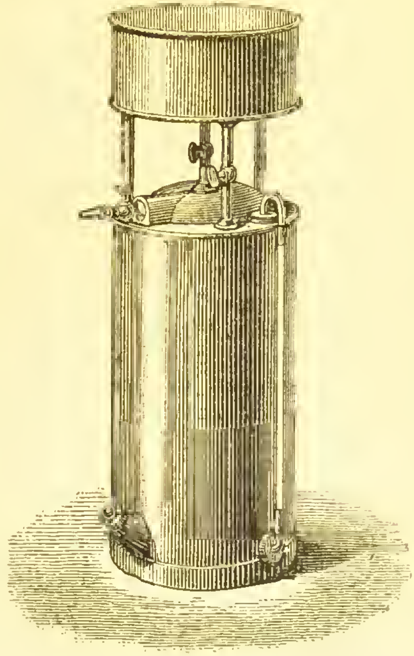
The vessel of water employed for the collection of gases which do not dissolve in water is usually spoken of as the pneumatic trough. It may be made of any material or of any dimensions to suit the nature of the experiment and the quantity of gas which is to be collected. When large jars are employed, it is necessary to provide a shelf upon which they can rest, with the mouth just below the surface of the water.

For storing and retaining larger quantities of gas Pepys' gas-holder is very convenient. It consists of a drum or reservoir of metal or of

* As a near approximation, it may be remembered that a litre of hydrogen weighs 0·09 gram, or 9 centigrams, and a gram of hydrogen occupies 11·2 litres.

glass, surmounted by a shallow trough or cistern, as shown in fig. 6, the communication between the two being made by a couple of tubes furnished with stop-cocks, one of which passes nearly to the bottom of the drum. A short wide open tube is inserted obliquely near the bottom of the vessel, into which a plug may be tightly screwed. A stop-cock near the top serves to transfer gas to a tube-apparatus. A glass water-gauge affixed to the side of the drum, and communicating with both top and bottom, indicates the level of the liquid within.

Fig. 6.



To use the gas-holder, the plug is first to be screwed into the lower opening, and the drum completely filled with water. All three stop-cocks are then to be closed and the plug removed. The pressure of the atmosphere retains the water in the gas-holder, and if no air-leakage occurs, very little water escapes. The extremity of the delivery-tube is now to be well pushed through the open aperture into the drum, so that the bubbles of gas may rise without hindrance to the upper part, displacing the water, which flows out in the same proportion into a vessel placed for its reception, or into a sink. When the drum is filled, or enough gas has been collected, the tube is withdrawn, and the plug screwed into its place.

Fig. 7.

When a portion of the gas is to be transferred to a jar, the latter is to be filled with water at the pneumatic trough, carried by the help of a basin or plate to the cistern of the gas-holder, and placed over the shorter tube. On opening the cock of the neighbouring tube, the column of water will cause compression of the gas, so that, on gently turning the cock beneath the jar, it will ascend into the latter in a rapid stream of bubbles. The jar, when filled, may again have the plate slipped beneath it, and may then be easily removed.

The use of gas-holders for laboratory purposes has become less common of late years, in consequence of the manufacture upon a large scale of several important gases, such as oxygen, hydrogen,

and carbon dioxide, and storage of them in cylindrical steel bottles, into which they are forced by powerful compressing pumps.

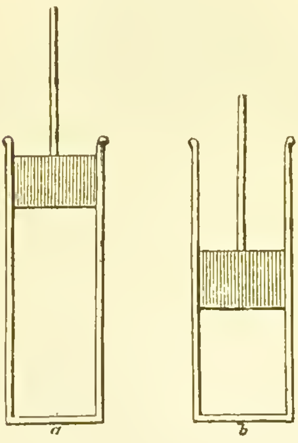
General Properties of Gases.

It requires some little abstraction of mind to realise completely the condition in which all things at the surface of the earth exist. We live at the bottom of an immense ocean of gaseous matter, which envelops everything, and presses upon everything with a force which appears, at first sight, perfectly incredible, but whose actual amount admits of easy proof.

Gravity being, so far as is known, common to all matter, it is natural to expect that gases, being material substances, should be acted upon by the earth's attraction, as well as solids and liquids. This is really the case, and the result is the weight or pressure of the atmosphere, which is nothing more than the effect of the attraction of the earth on the particles of air.

Gases, of which common air and hydrogen are examples, are in the highest degree elastic; the volume or space which a gas occupies depends upon the pressure exerted upon it. Let the reader imagine a cylinder, *a*, closed at the bottom, in which moves a piston air-tight, so that no air can escape between the piston and the cylinder. Suppose now the piston be pressed downwards with a certain force; the air beneath it will be compressed into a smaller bulk, the amount of this compression depending on the force applied; if the power be sufficient, the bulk of the gas may be thus diminished to one hundredth part or less. When the pressure is removed, the elasticity or *tension*, as it is called, of the included air or gas, will immediately force up the piston until it arrives at its first position.

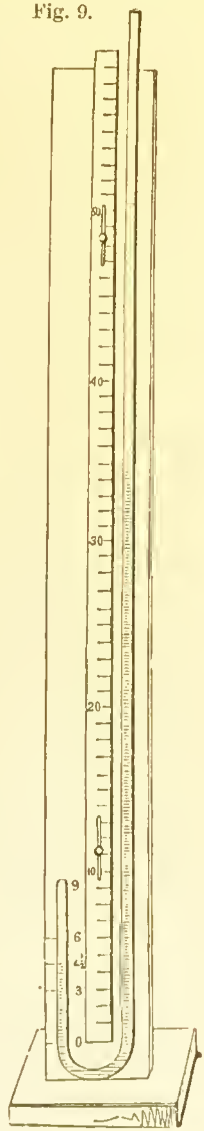
Fig. 8.



Again, take fig. 8, *b*, and suppose the piston to stand about the middle of the cylinder, having air beneath in its usual state. If the piston be now drawn upwards, the air below will expand, so as to fill completely the increased space, and this to an apparently unlimited extent. A volume of air, which, under ordinary circumstances, occupies the bulk of a cubic inch, might, by the removal of the pressure upon it, be made to expand to the capacity of a whole room, while a renewal of the former pressure would be attended by a shrinking down of the air to its former bulk. The smallest portion of gas introduced into a large exhausted vessel becomes at once diffused through the whole space, an equal quantity being present in every part;

the vessel is *full* although the gas is in a state of extreme tenuity. This power of expansion which air possesses may have, and probably has, in reality, a limit; but the limit is never reached in practice. We are quite safe in the assumption, that for all ordinary purposes of experiment air is perfectly elastic.

Fig. 9.



Relations between Pressure, Elasticity, and Volume of Gases.—It will now be necessary to consider a most important law which connects the volume occupied by a gas with the pressure made upon it, and is thus expressed :—

The volume of gas is *inversely* as the pressure ; the density and elastic force are *directly* as the pressure, and *inversely* as the volume.

For instance, 100 cubic inches of gas under a pressure of 30 inches of mercury would expand to 200 cubic inches were the pressure reduced to one-half, and shrink, on the contrary, to 50 cubic inches if the original pressure were doubled. The change of density must necessarily be in inverse proportion to that of the volume, and the elastic force follows the same rule.

The law of Boyle (1661), sometimes called the law of Mariotte, is easily verified by experiment. A glass tube about 7 feet long is closed at one end, and bent into the form represented in fig. 9, the open limb of the syphon being the longer. It is next attached to a board furnished with a movable scale of inches, and enough mercury is introduced to fill the bend, the level being evenly adjusted, and marked upon the board. Mercury is now poured into the tube until the enclosed air is reduced to one-half of its former volume ; and on applying the scale, it will be found that the level of the mercury in the open part of the tube stands very nearly 30 inches above that in the closed portion. The pressure of an additional "atmosphere" has consequently reduced the bulk of the contained air to one-half. If the experiment be still continued until the volume of air is reduced to a third, it will be found that the column measures 60 inches, and so in like proportion as far as the experiment is carried.

The above instrument is better adapted for illustration of the principle than for furnishing rigorous proof of the law. This has, however, been done. Arago and Dulong published, in the year 1830, an account of experiments made by them in Paris, in which

the law in question had been verified to the extent of twenty-seven atmospheres. With rarefied air also, of whatever degree of rarefaction, the law has been found true.

All gases are alike subject to this law, and all vapours of volatile liquids, when remote from their points of liquefaction.* It is a matter of the greatest importance in practical chemistry, since it gives the means of making corrections for pressure, or determining by calculation the change of volume which a gas would suffer by any given change of external pressure.

Let it be required, for example, to solve the following problem :—We have 100 cubic inches of gas in a graduated jar, the barometer standing at 29 inches ; how many cubic inches will it occupy when the column rises to 30 inches? Now the volume must be inversely as the pressure : consequently a change of pressure in the proportion of 29 to 30 must be accompanied by a change of volume in the proportion of 30 to 29, the 30 cubic inches of gas contracting to 29 cubic inches under the conditions imagined. Hence the answer—

$$30 : 29 = 100 : 96{\cdot}67 \text{ cubic inches.}$$

The reverse of the operation will be obvious. The student will do well to familiarise himself with the calculation of correction for pressure.

Relation between Temperature and Volume.—It has been shown that a given increase or diminution of pressure, when applied to a gas, produces a far greater change of volume than would be produced under the same circumstances in any solid or liquid. The volume of a given mass of a gas is also affected by change of temperature to a much greater extent than the volume of any solid or ordinary liquid by the same change of temperature. Formerly it was supposed that all gases expand at the same rate when heated (Law of Gay-Lussac). This, however, although approximately true, is not strictly so, and the rate of expansion of each gas is properly represented by a coefficient which is peculiar to itself, as is the case with solids and liquids. The following numbers, for example, represent the increase in the bulk of 1 volume of each gas for a rise of temperature from 0° to 1° centigrade.

Coefficients of Expansion for 1° *C.*

Air, ...	·003665
Hydrogen, ...	·003667
Carbon monoxide, ...	·003667
Nitrogen, ...	·003668
Nitrous oxide, ...	·003676
Carbon dioxide, ...	·003688
Cyanogen, ...	·003829
Sulphur dioxide, ...	·003845

* Near the liquefying point the law no longer holds ; the volume diminishes *more rapidly* than the theory indicates, a smaller amount of pressure being then sufficient. (See further, "Liquefaction of Gases").

The rate of expansion, then, in the more permanent gases like air, approximates to ·00366 per centigrade degree, or $\frac{1}{273}$ of the volume starting from 0°.

It will be noticed that the greatest deviations from this value are exhibited by those gases which, as will hereafter be shown, are most easily liquefied, such as carbon dioxide, cyanogen, and sulphur dioxide.

Passing down the scale of temperature from zero, contraction occurs at the same rate, so far as it has been possible to observe. At 273 degrees below freezing point, therefore, the volume of a gas would become reduced to nothing, if it could be conceived that no change supervenes in its physical condition. All gases condense into liquids before this temperature is reached. This consideration, however, possesses some theoretical and even practical interest, inasmuch as it enables us to express very concisely the relation of the volume of a gas to temperature. For, calling $-273°$ centigrade the zero of *absolute temperature*, we may say that the volume of a gas is proportional to the absolute temperature.

In the practical manipulation of gases, it very often becomes necessary to make a correction for temperature, or to discover how much the volume of a gas would be increased or diminished by a particular change of temperature. The calculation can easily be made as follows. The differences in the rate of expansion of different gases being so small, we may, for ordinary purposes, assume that the rates of expansion are all the same, and are equal to the value already given, viz., ·00366 or $\frac{1}{273}$. Then, since 273 volumes of a gas at 0° C. become $273+t$ when the temperature is $t°$, and $273+T$ when the temperature is T°, the rule is very easily applied. Or using the decimal coefficient, V volumes of gas at 0°, become $V+·00366\,V$, or $V\,(1+·00366)$ at 1°, and generally $V\,(1+·00366t)$, when the temperature is $t°$.

If this calculation is required to be made on the Fahrenheit scale, it must be remembered that the zero of that scale is 32° below the melting-point of ice. Above this temperature the expansion for each degree of the Fahrenheit scale is $\frac{1}{460}$ of the original volume.

This, and the correction for pressure, are operations of very frequent occurrence in chemical investigations, and the student will do well to become familiar with them.

The following formula includes both these corrections:—Let V and V′ be the volume of a gas at the temperatures t and t' centigrade, and under the pressures p and p', measured in millimetres of mercury: then

$$\frac{V}{V'}=\frac{1+0·00366t}{1+0·00366t'}\cdot\frac{p'}{p}.$$

The case which most frequently occurs is the reduction of a measured volume, V, of a gas at the temperature t and pressure p to the volume V_0, which it would occupy at 0° C., and under a pressure of 760 mm. In this case, we have $t'=0$, and $p'=760$, therefore—

$$\frac{V}{V_0} = (1+0{\cdot}00366t) \cdot \frac{760}{p},$$

and

$$V_0 = \frac{V}{1+0{\cdot}00366t} \cdot \frac{p}{760}.$$

Diffusion of Gases.

When a gas is placed in a jar or bottle, if the mouth be not closed by a stopper or plate of glass, the gas will escape and mix with the air even in opposition to the effects of gravity, and independently of differences of temperature which would give rise to convection currents. The spontaneous escape of the gas and the entrance of air into the bottle in such a case are both due to the operation of gaseous diffusion. This remarkable phenomenon was first particularly noticed about 1829 by Doebereiner, who found that when hydrogen gas was collected in the usual way over water, in a certain jar which was left standing in the pneumatic trough, the water rose inside the jar, indicating a diminution in the volume of the gas. The jar used was afterwards found to have a minute crack in the glass. Graham afterwards examined the facts and gave the explanation.

The interdiffusion of two gases can easily be demonstrated by many experiments. If two bottles containing gases which do not act chemically upon each other at common temperatures be connected by a narrow tube and left for some time, the gases after a certain time, depending much upon the narrowness of the tube and its length, will be found uniformly mixed, even though they differ greatly in density, and the system has been arranged in a vertical position with the heavier gas downwards. Oxygen and hydrogen can thus be made to mix, in an hour, against the action of gravity, through a tube a yard long, and not more than one-quarter of an inch in diameter: and the same is true of all other gases which do not act directly upon each other.

If a vessel be divided into two portions by a diaphragm or partition of porous earthenware or dry plaster of Paris, and each half of it filled with a different gas, diffusion will immediately commence through the pores of the dividing substance, and will continue until perfect mixture has taken place. All gases, however, do not permeate the same porous body, or, in other words, do not pass through narrow orifices, with the same degree of facility. Graham established the existence of a very simple relation between the rapidity of diffusion and the density of the gas, which is expressed by saying that the *rate of diffusion varies inversely as the square root of the density of the gas.* Thus, in the experiment supposed, if one-half of the vessel be filled with hydrogen and the other half with oxygen, the two gases will penetrate the diaphragm at very different rates, 4 cubic inches of hydrogen passing into the oxygen side, while 1 cubic inch of oxygen travels in the opposite direction. The densities of the two gases are to each other in the proportion of

1 to 16; their relative rates of diffusion are inversely as the square roots of these numbers, *i.e.*, as 4 to 1.

The simplest and most striking method of exhibiting the phenomenon of diffusion is by the use of Graham's diffusion-tube, which, in its original form consisted of a piece of wide glass tube 10 or 12 inches long, having one of its extremities closed by a plate of plaster of Paris, about half an inch thick, and well dried. When the tube is filled by displacement with hydrogen, and then set upright in a glass of water, the level of the liquid rises in the tube so rapidly that its movement is apparent to the eye, and speedily attains a height of several inches above the water in the glass. The gas is actually rarefied by its superior diffusive power over that of the external air. A more effective form of apparatus is shown in fig. 10, and consists of a clay battery cylinder closed by a sound cork, through which passes a narrow glass tube, dipping into a vessel of coloured water. If a glass full of hydrogen or other light gas is inverted over the cylinder, bubbles of air rapidly escape from below, and after this has continued for a minute or two, the removal of the reservoir of hydrogen is followed immediately by the ascent of liquid in the tube. In every experiment of this kind an interchange is going on between the gas within and the air without. As the hydrogen escapes air enters, but at a less rapid rate.

Fig. 10.

This property of gases has doubtless some important influence in Nature, as it must assist in maintaining uniformity in the composition of the atmosphere, in promoting evaporation of water, and preventing local accumulation of gases.

A partial separation of gases and vapours of unequal diffusibility may be effected by allowing the mixture to permeate a plate of graphite or porous earthenware into a vacuum. This effect, called a t m o l y s i s, is exhibited by means of the *tube atmolyser*. This is simply a narrow tube of unglazed earthenware, such as a tobacco-pipe stem, of suitable length, which is placed within a shorter tube of glass, and secured in its position by corks. The glass tube is connected with an air-pump, and the annular space between the two tubes is made as nearly vacuous as possible. Air or other mixed gas is then allowed to flow along the clay tube in a slow stream, and collected as it issues. The gas or air atmolysed is, of course, reduced in volume, much gas penetrating through the pores of the clay tube into the air-pump vacuum, and the lighter gas diffusing the more rapidly, so that the proportion of the denser constituent is increased in the gas collected. In one experiment, the proportion of oxygen in the air, after traversing the atmolyser, was increased from 20·8 per cent., which is the normal proportion, to 24·5 per cent. With a mixture of oxygen and hydrogen, the separation is, of course, more considerable.

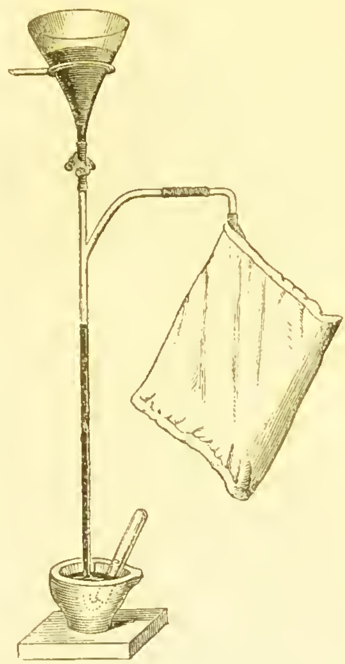
A distinction must be carefully drawn between real diffusion through small apertures, and the apparently similar passage of gases through membranous diaphragms, such as caoutchouc, bladder, gold-beater's skin, etc. In this mode of passage the rate of interchange depends partly on the relative diffusibilities of the gases; partly on the different degrees of adhesion exerted by the membrane on the different gases, by virtue of which the gas which adheres most powerfully penetrates the diaphragm most easily, and, attaining the opposite surface, mixes with the other; and partly, it has been supposed, on an actual liquefaction of the gases, which then penetrate the membrane (as ether and petroleum do), and may again evaporate on the surface and appear as gases. A sheet of caoutchouc tied over the mouth of a wide-mouthed bottle filled with hydrogen, is soon pressed inwards, even to bursting. If the bottle be filled with air, and placed in an atmosphere of hydrogen, the swelling and bursting takes place outwards. If the membrane is moist, the result is likewise affected by the different solubilities of the gases in the water or other liquid which wets it. For example, the diffusion of carbon dioxide into atmospheric air is very slow, but it passes into the latter through a wet bladder with the utmost ease, in virtue of its solubility in the water with which the membrane is moistened. It is by such a process that the function of respiration is performed: the aëration of the blood in the lungs and the disengagement of the carbon dioxide are effected through wet membranes; the blood is never brought into actual contact with the air, but receives its supply of oxygen, and is relieved of excess of carbon dioxide by this kind of spurious diffusion. The high diffusive power of hydrogen against air renders it impossible to retain that gas for any length of time in a bladder or caoutchouc bag: it is even unsafe to keep it long in a gas-holder, lest it should become mixed with air by slight accidental leakage, and rendered explosive.

The unequal absorption of gases in the manner above mentioned often effects a much more complete separation of the components of a gaseous mixture than can be attained by the atmolytic method above described. Graham has shown that oxygen is absorbed and condensed by caoutchouc two-and-a-half times more abundantly than nitrogen, and that when one side of a caoutchouc film is freely exposed to the air, while a vacuum is produced on the other side, the film allows a gas containing 41·6 per cent. of oxygen to pass through, instead of the 21 per cent. usually present in the air.

The apparatus by which this interesting result may be produced is shown in fig. 11. Two sheets of unvulcanised india-rubber, having a piece of common carpet between to prevent adhesion, are joined at the edges, so as to make a flat bag, one corner of which can be attached by a glass tube to the Sprengel mercury pump. The latter consists of a reservoir of mercury surmounting a vertical tube, which must be more than 30 inches high, with a side branch as shown in the figure. Upon allowing mercury to drop slowly from

the funnel, it draws with it air from the side tube, and carries it down in separate portions, which can be collected in an inverted tube below. If the bag be exhausted of air in this manner, and the pump be kept working, gas is slowly extracted, and, after an hour or two, the air which passes through is found to be so rich in oxygen that it is capable of rekindling a charred wood splint with tip still red hot.

Fig. 11.



Even metals possess this power of absorbing large quantities of gases. Deville and Troost observed the remarkable fact that hydrogen gas is capable of penetrating platinum and iron tubes at a red heat, and Graham suggested that this effect may be connected with a power possessed by these and certain other metals to absorb hydrogen, possibly in its character as a metallic vapour. Platinum in the form of wire or plate, at a low red heat, can take up 3·8 volumes of hydrogen measured cold, and palladium foil condenses as much as 643 times its volume of hydrogen at a temperature below 100° C. In the form of sponge, platinum was found to absorb 1·48 times its volume of hydrogen, and palladium 90 volumes. This absorption of gases by metals is called o c c l u s i o n.

The meteoric iron of Lenarto contains a considerable quantity of occluded hydrogen. When heated in a good vacuum, it yields 2·85 times its volume of gas, of which 85·68 per cent. consists of hydrogen, with 4·46 carbon monoxide and 9·86 nitrogen. Now, hydrogen has been recognised by spectrum analysis in the light of the fixed stars, and constitutes the principal element in the atmosphere of a numerous class of stars. "The iron of Lenarto," says Graham, "has, no doubt, come from such an atmosphere, in which hydrogen greatly prevailed. This meteorite may therefore be looked upon as holding imprisoned within it, and bringing to us, the hydrogen of the stars."

The rates of e f f u s i o n of gases, that is to say, their rates of passage through a minute aperture in a thin plate of metal or other substance into a vacuum, follow the same law as their rates of diffusion, that is to say, they are inversely as the square roots of the densities of the gases. Nevertheless, the phenomena of diffusion and effusion are essentially different in their nature, the effusive movement affecting masses of a gas, whereas in the diffusive move-

ment molecules are concerned; and a gas is usually carried by the former kind of impulse with a velocity many thousand times greater than by the latter. Mixed gases are effused at the same rates as one gas of the actual density of the mixture: and no separation of the gases occurs, as in *diffusion* into a vacuum.

The law of effusion just stated is true only under the condition that the gas shall pass through a minute aperture in a very thin plate. If the plate be thicker, so that the aperture becomes a tube, very different rates of efflux are observed; and when the capillary tube becomes considerably elongated, so that its length exceeds its diameter at least 400 times, the rates of flow of different gases into a vacuum again assume a constant ratio to each other, following, however, a law totally distinct from that of effusion.

OXYGEN.

Symbol O. Atomic weight, 16. Density, 16, approximately.

Oxygen was discovered in the year 1774 by Priestley, and about two years earlier by Scheele, in Sweden, independently of each other.

Scheele's work was not published till some time after the discovery of Priestley was made known. Scheele described the gas under the name *fire-air*, Priestley called it *dephlogisticated air*. The name *oxygen** was given to it by Lavoisier some time afterwards.

Oxygen exists in a free and uncombined state in the atmosphere, mixed with another gaseous body, nitrogen. It is usually obtained for purposes of experiment by decomposing certain metallic oxides and salts.

The source from which it was originally obtained by Priestley is the red oxide of mercury, or "red precipitate" of the old writers, which is resolved by heat into oxygen gas and metallic mercury.

$$2HgO = 2Hg + O_2.$$

Scheele's first process consisted in heating nitric acid, but he also obtained it by heating black oxide of manganese and red precipitate of mercury, as well as oxides of silver and gold. Oxide of manganese requires a red heat for its decomposition, and gives up not more than about one-third of the oxygen it contains, the residue consisting of a lower oxide of manganese. Thus—

$$4MnO_2 = 2Mn_2O_3 + O_2,$$

or

$$3MnO_2 = Mn_3O_4 + O_2.$$

A method more convenient than either of these depends upon the decomposition of potassium chlorate by heat. This salt, when heated

* From ὄξος, vinegar, *i.e.*, acid, and γεν, a root signifying production.

alone, yields pure oxygen gas, and if the temperature is pretty high and maintained long enough, the residue which is left consists wholly of potassium chloride. Thus—

$$2KClO_3 = 2KCl + 3O_2.$$

If the operation be interrupted before all the oxygen is expelled, the residue will be found to contain more or less of potassium perchlorate, $KClO_4$.

When it is not essential that the oxygen obtained should be quite pure—as, for example, when required for use in the oxyhydrogen lamp—the chlorate of potassium may be mixed with about one-tenth of its weight of dry peroxide of manganese. When this mixture is heated, the oxygen is disengaged much more readily and rapidly than when the chlorate is used alone. The chlorate is wholly reduced to chloride of potassium, the manganese oxide remaining undiminished and apparently unchanged. There can be little doubt, however, that the latter undergoes a succession of changes in which the elements of the chlorate are concerned, for the gas evolved contains a notable quantity of chlorine, and the residue a corresponding amount of oxide of potassium. This effect is an instance of the kind of action which is sometimes called a "catalytic" action, in which a limited quantity of one body is capable of promoting a change in an indefinite quantity of another body with which it is in contact. Other examples will occur later on.

Another process, which is now worked upon a manufacturing scale, has been patented by M. M. Brin. Atmospheric air, freed from dioxide carbon, is pumped under slight pressure into retorts containing anhydrous oxide of barium (baryta), heated to about 700°. Here a portion of the oxygen is absorbed, while the nitrogen passes on and escapes. After a few minutes the pressure in the retorts is reduced below atmospheric pressure, the temperature remaining unchanged. Oxygen is then evolved and is drawn by the pump from the retorts and delivered into the oxygen-holder. After the liberation of the absorbed oxygen, the baryta is left ready for a repetition of the process.

Oxygen is, bulk for bulk, a little heavier than atmospheric air, its density being 15·88 referred to that of hydrogen as unity.* A litre of oxygen at the standard temperature and pressure, that is to say, at 0° C., and 760 millimetres barometric pressure, weighs 1·42285 gram. At 15·5° C. (60° F.), and under a pressure of 30 inches, 100 cubic inches of the gas weigh 34·29 grains.

Oxygen at a temperature below − 118·8° and under a pressure of 51 atmospheres forms a pale blue liquid which is pretty strongly attracted by a magnet. It is in this condition chemically inactive, probably on account of the low temperature, so that phosphorus and other easily oxidisable substances placed in contact with it are unaffected. Its boiling point under atmospheric pressure is − 182·7°.

Oxygen is the sustaining principle of animal life, and of all the

* Rayleigh, *Proc. Roy. Soc.*, Feb. 1892.

ordinary phenomena of combustion. Bodies which burn in the air burn with greatly increased splendour in oxygen gas. If a taper be blown out, and then introduced, while the wick remains red-hot, it is instantly rekindled ; a slip of wood or a match is relighted in the same manner. This effect is highly characteristic of oxygen, there being but one other gas which possesses the same property ; and this is easily distinguished by other means. The experiment with the match is also constantly used as a rude test of the purity of the gas when it is about to be collected from the retort, or when it has stood for some time in contact with water exposed to air.

When a bit of charcoal is affixed to a wire, and plunged with a single point red-hot into a jar of oxygen it burns with great brilliancy, throwing off beautiful scintillations, until, if the oxygen be

Fig. 12.

in excess, it is completely consumed. A bundle of steel wires armed at its extremity with a bit of lighted charcoal, and introduced into a vessel of oxygen gas, burns with great brilliancy. If the experiment be made in a jar standing on a plate, the fused globules of black iron oxide fix themselves in the glaze of the latter, after falling through a stratum of water half an inch in depth. Kindled sulphur burns with great beauty in oxygen ; and phosphorus, under similar circumstances, exhibits a splendour which the eye is scarcely able to support. In each case the burning body enters into combination with the oxygen, forming an oxide.

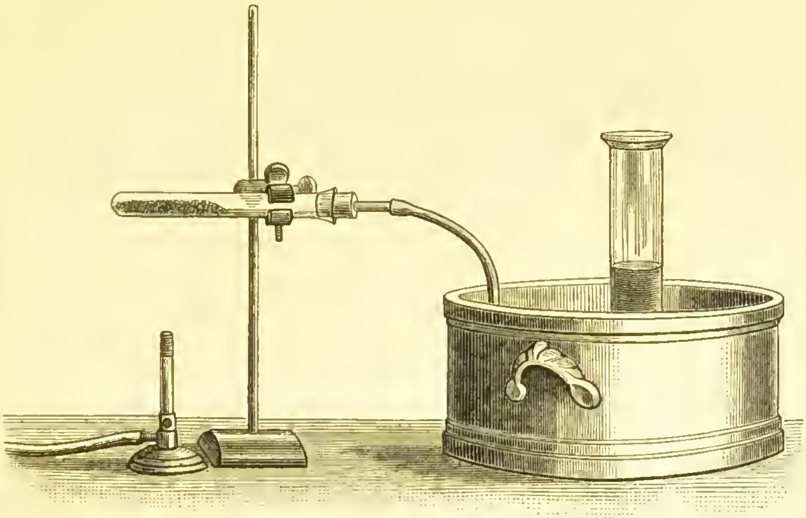
When a compound burns in atmospheric air, the same ultimate effect is produced as in pure oxygen ; the action is, however, less energetic, in consequence of the presence of nitrogen, which dilutes the oxygen and weakens its chemical powers. The process of respiration in animals is an effect of the same nature as ordinary combustion. The blood contains substances which slowly burn by the aid

of the oxygen thus introduced into the system. When this action ceases, life becomes extinct.

Experiments.—1. Place in a test-tube, or better, a short piece of "combustion" tubing, of which one end has been sealed up like that of a test-tube, a small quantity of red mercuric oxide, and, holding the tube by the fingers at the upper part, apply the flame of a Bunsen burner to the bottom till a grey crust begins to form higher up on the side of the tube. Now, take a slip of wood, set fire to one end, and when charred, blow out the flame, leaving a few sparks upon the blackened extremity. Introduce this into the test-tube, which should now be full of oxygen. The wood will be rekindled into flame.

A similar experiment may be made with red lead, a substance formed by roasting in the air, at a temperature short of redness, the

Fig. 13.



protoxide of lead or litharge, PbO. It may thus be shown that oxygen can be withdrawn from the atmosphere and reproduced in a state of purity unmixed with nitrogen or any other gas.

2. Place in a test-tube a few grams of potassium chlorate. Apply heat in the same way. The salt first crackles, then melts, and finally appears to boil. When in this condition oxygen is being disengaged from it, and when tested with the match rekindles it as before.

3. Mix about 10 grams of potassium chlorate in coarse powder with about 1 gram of manganese dioxide, place the mixture in a test-tube to which has been previously fitted a cork and tube bent as shown in figure 13.

The tube is held in a nearly horizontal position by the clamp of a small retort stand. The end of the tube dips under water in such a

position that the gas which will issue from it may be discharged into the jar filled with water placed for its reception. Now apply a very gentle heat to the upper part of the black powder in the tube. Oxygen soon comes off freely, and several jars should be ready for collecting as much as may be required. When a sufficient quantity has been obtained, remove the delivery-tube from the water. Cover the mouth of each jar as removed from the water with a glass plate, or close it by a stopper. Ten grams of potassium chlorate will yield about $2\frac{1}{2}$ litres of oxygen, or nearly 5 pints.

4. Attach a piece of charcoal to a wire, ignite it in a flame, then dip it into one of the jars filled with oxygen.

5. Place a little sulphur in a "deflagrating" spoon, set fire to it, and, while burning, plunge it into oxygen.

6. Burn off any sulphur remaining upon the spoon from the previous experiment; while the spoon is cooling, refer to the article on phosphorus for the precautions necessary in dealing with that dangerous substance. Cut off a piece of phosphorus half the size of a pea, dry it on filter-paper, and place in the deflagrating spoon. Ignite the phosphorus by touching it with a heated wire or glass rod, and immediately plunge it into oxygen.

7. When sufficiently cool, pour a little distilled water into each of the three jars used in the combustion of charcoal, sulphur, and phosphorus. Then dip a piece of blue litmus paper into each. It will be turned red, indicating that an acid has been formed.

NITROGEN.

Symbol, N''' Atomic weight, 14. Density, 14.

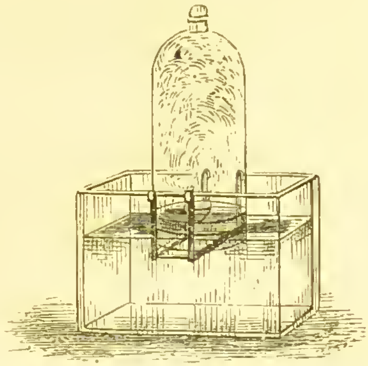
Nitrogen* constitutes about four-fifths of the atmosphere, and enters into a great variety of combinations. It may be prepared by several methods. One of the simplest of these is to burn out the oxygen from a confined portion of air by phosphorus, by copper, or by a jet of hydrogen.

Experiment.—A small porcelain capsule is floated on the water of the pneumatic trough, and a piece of phosphorus is placed in it and set on fire. A bell-jar is then inverted over the whole, and suffered to rest on the shelf of the trough, so as to project a little over its edge. At first the heat causes expansion of the air of the jar, and a few bubbles are expelled, after which the level of the water rises considerably. When the phosphorus becomes extinguished by exhaustion of the oxygen, and time has been given for the subsidence of the cloud of finely divided snow-like phosphoric oxide which

* *I.e.*, Generator of nitre; also called, chiefly by French chemists, *Azote*, from *α*, privative, and *ζωή*, life.

floats in the residual gas, the nitrogen may be transferred into another vessel, and its properties examined. Prepared by the foregoing process, nitrogen is contaminated with a little vapour of phosphorus, which communicates to the gas its peculiar odour.

Fig. 14.



Experiment. — A preferable method is to fill a tube with turnings of copper or copper gauze; to heat this tube to redness; and then pass through it a slow stream of atmospheric air, the oxygen of which is entirely removed, during its progress, by the heated copper. The apparatus shown in fig. 3, p. 22, may be used for this purpose. The iron tube is packed with copper turnings instead of iron. The flask or can contains no water, but only air. By attaching to the vertical open tube a piece of flexible pipe connected with the water supply, and turning on a very slow stream of water, the air may be made to flow through the red-hot copper, where the oxygen is retained, whilst the nitrogen passes on into the gas jar standing in the pneumatic trough.

When chlorine gas is passed into solution of ammonia, the latter substance, which is a compound of nitrogen with hydrogen, is decomposed; the chlorine combines with the hydrogen, and the nitrogen is set free, with effervescence. In this manner very pure nitrogen can be obtained. In making this experiment, it is necessary to stop short of saturating or decomposing the whole of the ammonia, otherwise there will be great risk of accident from the formation of an exceedingly dangerous explosive compound, produced by the contact of chlorine with an ammoniacal salt.

Another very easy and perfectly safe method of obtaining pure nitrogen is to decompose ammonium nitrite. On boiling a solution of potassium nitrite with sal-ammoniac, nitrogen gas is evolved, while potassium chloride remains in solution. The reaction is represented by the equation,

$$KNO_2 + NH_4Cl = KCl + 2H_2O + N_2.$$

Nitrogen is destitute of colour, taste, and odour; it is a little lighter than air, its density being 0·972. A litre of the gas at 0° C. and 760 mm. barometric pressure weighs 1·2505 gram (Rayleigh). 100 cubic inches, at 60° F. and 30 inches barometer, weigh about 30 grains. Nitrogen is incapable of sustaining combustion or animal life, although, like hydrogen, it has no positive poisonous properties; neither is it soluble to any notable extent in water or in caustic alkali; it is, in fact, best characterised by negative properties.

Experiment.—Having prepared some nitrogen gas by one of the

methods described above, decant a portion of it into a gas cylinder, close the mouth of this with a glass plate, remove it from the water, and introduce a lighted taper. The flame is extinguished.

Experiment.—Collect a second cylinder full of the gas, and pour into it a little clear lime-water. The lime-water shaken up with the gas does not become cloudy. This test serves to distinguish nitrogen from carbon dioxide. The atter gas also differs from nitrogen by its greater density.

Atmospheric Air.—The exact composition of the atmosphere has repeatedly been made the subject of experimental research. Beside nitrogen and oxygeu, the air contains a little carbon dioxide (carbonic acid gas), a very variable proportion of aqueous vapour, a trace of ammonia, and under certain circumstances nitric acid and ozone. It also contains nearly 1 per cent. of a remarkable gas, called argon, discovered in 1894 by Lord Rayleigh and Professor Ramsay. The oxygen and nitrogen are in a state of mixture, not of combination, yet their ratio is remarkably uniform. Air has been brought from lofty alpine heights, and compared with that from the plains of Egypt; it has been brought from an elevation of 21,000 feet by the aid of a balloon; it has been collected and examined in Loudon and Paris, and many other places: still the proportion of oxygen and nitrogen remains nearly unaltered, the wind, together with the diffusive energy of the gases, being adequate to maintain this perfect uniformity of mixture. The carbon dioxide, on the contrary, being much influenced by local causes, varies considerably.

Composition of the Atmosphere.

	By weight.	By measure.
Nitrogen (including 1 p.c. argon), .	77 parts	79·19
Oxygen, ...	23 „	20·81
	100	100·00

Carbon dioxide, from 3·7 measures to 6·2 measures in 10,000 measures of air.
Aqueous vapour variable, depending much upon the temperature.
Ammonia and nitric acid, traces.
Ozone or hydrogen peroxide, traces in country air.

Dr Frankland has analysed samples of air taken by himself in the valley of Chamouni, on the summit of Mont Blanc, and at the Grands Mulets. The following are the results of his analyses expressed as volumes per cent.

	Carbon Dioxide.	Oxygen.
Chamouni (3000 feet), . .	0·063	20·894
Grands Mulets (11,000 feet), .	0·111	20·802
Mont Blanc (15,732 feet), . .	0·061	20·963

Beside the gaseous ingredients present in normal uncontaminated air, the dust which is always present contains an immense diversity of solid substances, partly earthy or siliceous, partly of organic origin, including the germs of moulds and other micro-organisms which are now known to play a very important part in relation to the life of higher animals and plants, and even in processes previously assumed to be purely chemical. In towns the proportion of carbon dioxide generally exceeds the normal amount, and in crowded buildings may reach 20 or 30 volumes per 10,000 of air ; it is always accompanied by putrescent organic matters which are more deleterious to health than carbon dioxide. The employment of coal as fuel leads to the production of an appreciable quantity of sulphuretted hydrogen and of sulphurous and sulphuric acids, which, being brought down by the rain, cause much injury to stone work, metals, and painted surfaces.

A litre of pure and dry air at 0° C. and 760 mm. pressure weighs 1·29366 grams. 100 cubic inches at 60° F. and 30 inches barom. weigh 30·935 grains ; hence a cubic foot weighs 536·96 grains, which is $\frac{1}{816}$ of the weight of a cubic foot of water at the same temperature.

The analysis of air by weight was effected by Dumas and Boussingault, in 1841, by passing it over finely divided copper contained in a tube of hard glass, carefully weighed, and then heated to redness : the nitrogen was suffered to flow into an exhausted glass globe, also previously weighed. The increase in weight of the copper after the experiment gave the amount of oxygen, and the increase in weight of the exhausted globe gave the nitrogen.

The analysis of air by volume was formerly effected by admitting small successive quantities of nitric oxide into a graduated tube containing the sample of air standing over water, and observing the diminution of volume which resulted. This, however, is a process by which no accurate estimations could be effected, and subsequently it was found that better results could be obtained by the action of phosphorus, or by explosion with hydrogen.

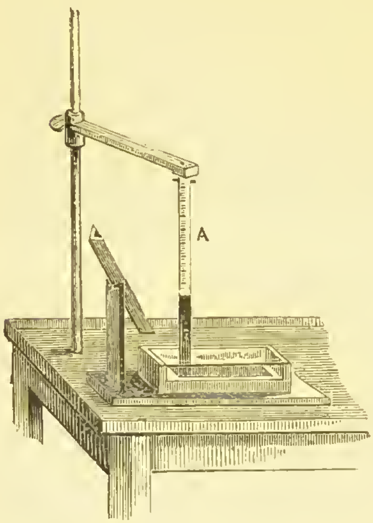
Experiment.—Collect in a graduated tube by displacement of water, 100 to 200 cc. of the air to be examined, and then pass up into the gas a short stick of clean phosphorus affixed to the end of a wire. If the whole is left for about twenty-four hours, the oxygen is slowly but completely absorbed, the phosphorus is then withdrawn, and the volume of residual nitrogen can be read off.

The most accurate method is to mix the air with hydrogen and pass an electric spark through the mixture : after explosion the volume of gas is read off and compared with that of the air employed. Since the analysis of gaseous bodies by explosion is an operation of great importance, it may be worth while to describe the process in detail, as it is applicable, with certain obvious variations, to a number of analogous cases.

Instruments for this purpose are called e u d i o m e t e r s. The simplest, and, on the whole, the most convenient, consists of a straight graduated glass tube (A, fig. 15) closed at the top, and having

platinum wires inserted near the closed end, to give passage to an electric spark. This tube is filled with mercury, and inverted in a mercurial pnueumatic trough.

Fig. 15.



For the analysis of air, a quantity sufficient to fill about one-sixth of the tube is introduced, and its volume accurately ascertained by reading off with a telescope the number of divisions on the tube to which the mercury reaches, whilst the height of the column of mercury in the tube above the trough, together with that of the barometer, and the temperature of the air, are also read off. A quantity of pure hydrogen gas is now added, more than sufficient to unite with all the oxygen present (about half the volume of the air), and the volume of the gas and the pressure exerted upon it are determined as before. An electric spark is now passed through the mixture, care being taken to prevent any escape, by pressing the open end of the eudiometer against a piece of sheet caoutchouc under the mercury in the trough. After the explosion, the volume is again determined, and is found to be less than that before the explosion. The volume of gas read off must in each case be reduced to standard pressure and temperature by the method already given (pp. 28, 29).

Now, since the hydrogen is in excess, and 2 volumes of that gas unite with 1 volume of oxygen to form water, one-third of the diminution must be the volume of the oxygen contained in the air introduced. An example will render this clear :—

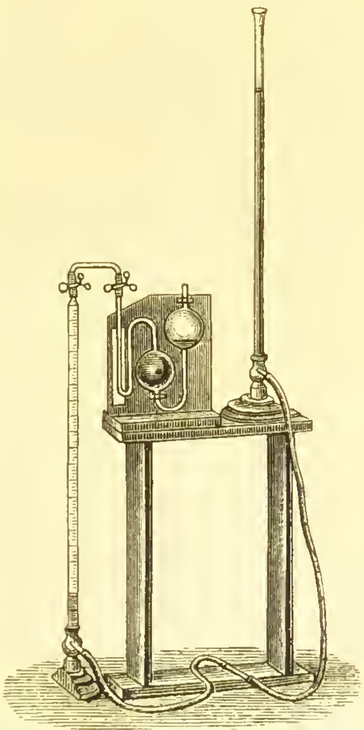
Air introduced, ...	100 measures.
Air and hydrogen, ...	160
Volume after explosion, . . .	97
Diminution, ...	63

$$\frac{63}{3} = 21 = \text{oxygen in the 100 measures.}$$

Various modifications of the apparatus employed in this method have been devised with the object of saving time in the process: a description of these will be found in special works on gas analysis.

When the greatest accuracy is not essential, but saving of time is a matter of importance, another form of apparatus, devised by Hempel, may be used for the analysis of air, and generally of gaseous mixtures in which no ingredient is present in merely minute quantity. It has the advantage of dispensing with the use of mercury, and is frequently used for the analysis of chimney gases from boiler furnaces, and for other purposes in connection with manufactures. This apparatus, like several others constructed upon a similar principle, consists essentially of two parts, namely, the absorption apparatus, in which the gas is brought into contact with reagents, and the apparatus for measurement. These are represented in the accompanying figure 16. A vertical measuring-tube, graduated into cubic centimetres, is connected at the bottom by flexible tubing to a second ungraduated open tube, placed upon a separate stand. The open tube is filled with water, and when raised into such a position as shown in the figure, the water tends to drive any enclosed gas through the capillary tube at the top, when the pinch tap, which compresses the rubber joint, is relaxed. Conversely, gas may be drawn back by simply lowering the open tube and relaxing the pinch tap. The absorption apparatus consists of two or more bulbs in which can be placed strong solution of potash, solution of pyrogallol, or other reagents, with which the gas may be brought into contact by passing from the measuring tube in the manner described. It is usual to keep ready several sets of absorption bulbs charged with the reagents required. The pressure upon the gas when it is measured, is reduced to atmospheric pressure by holding the water tube in such a position that the surface of the water in both tubes is at the same level. To determine the temperature, a thermometer suspended near gives it with sufficient accuracy for most technical purposes, but it may be regulated more exactly by surrounding the measuring tube by a wider glass tube filled with water, like the jacket of a Liebig condenser, in which a thermometer may be placed.

Fig. 16.

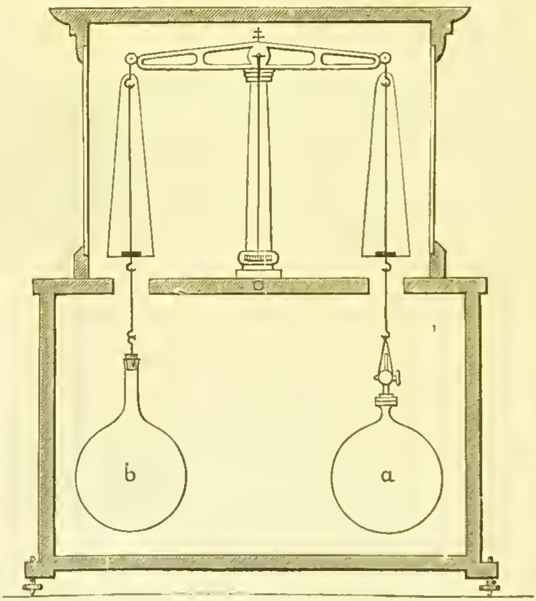


It has already been stated that the oxygen and nitrogen in atmospheric air are merely mixed together mechanically and are not chemically united. This, however, was not always recognised, and

it may therefore be useful to the student to explain briefly the reasons which have led to this conclusion.

In the first place, although the proportion of oxygen is nearly constant, it is not absolutely so, and since chemical compounds are of fixed composition, the ratio of their elements to one another being quite constant, air cannot be a chemical compound. Further, if we attempt to express the relative quantities of oxygen and nitrogen in *atomic* proportions, we find the formula very complicated and entirely unlike the formula of any other known compound of two elements. We may mix together oxygen and nitrogen gases in the proportions in which they occur in atmospheric air, and the mixture

Fig. 17.



possesses all the common physical and chemical properties of air which has been deprived of water and carbon dioxide, but in the process of mixture the two gases show no signs of chemical action, such as the evolution or absorption of heat or change of volume which is usually observed in the formation of chemical compounds by union of gases. Another sort of indication is obtained from observation of the fact that in air the oxygen and nitrogen preserve their specific properties independently of each other. Thus when air is exposed to contact with water the oxygen dissolves more freely than the nitrogen, and the dissolved portion of the air is richer in oxygen than the residual portion. This will be explained at length on a later page (*see* "Absorption of Gases"). The phenomena of diffusion may also be turned to account as well as the dialytic passage of gases through india rubber, and in all these cases, as already explained (pp. 32-33),

a partial separation of the oxygen from the nitrogen is producible by means which do not involve any chemical process.

Determination of the Relative Densities of Gases and Vapours.

Reference having already been made to the relative densities of several gases, and as some of the fundamental doctrines of chemistry are based upon a knowledge of these relations, a brief description must be given of the chief methods employed for their determination.

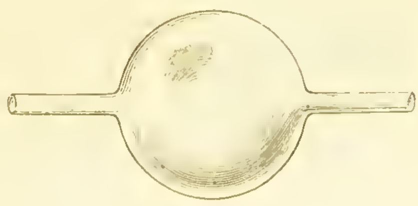
The method employed by Regnault, and later by Lord Rayleigh, for the determination of the relative densities of gases, is based upon a very simple principle. A large glass globe is filled with the gas in a pure state, and at a known temperature and pressure. In order to avoid corrections as much as possible, the globe in which the gas is weighed is counterpoised by a similar globe as nearly as possible equal to it in size and weight. The two globes are suspended in a glass case beneath the balance as shown in figure 17.

In order to determine the weight of the gas, it is necessary to add to the observed weight, the weight of an equal volume of air at the same temperature and pressure; that is to say, the air displaced by the gas. The sum of these weights divided by the weight of the air gives a quotient which is the density of the gas compared with the air as unit. If it is desired to express the density in relation to hydrogen, the value must be multiplied by 14·42.

Experiment.—Although the accurate determination of the densities of gases, especially of those which are comparatively light, is not within the capacity of inexperienced students, a sufficient approximation to the density of heavier gases may be easily attained even by beginners in the following manner:—

Two globes are taken of the form shown in figure 18, and the tubes fitted with stoppers made of a piece of rubber tube closed at one end. The globes should be chosen so as to have as nearly as possible the same capacity and weight, the one being used as the counterpoise of the other, final adjustment of the weight being made by the use of lead foil or small shot. The capacity of the globe, which is to be filled with the gas, must have been determined once for all by filling it with water and weighing or running out the water into a measuring vessel. The globe must, of course, be dried before attempting to counterpoise it or fill it with gas. If the gas is heavier than air it is admitted into one tube, while the other is directed vertically

Fig. 18.

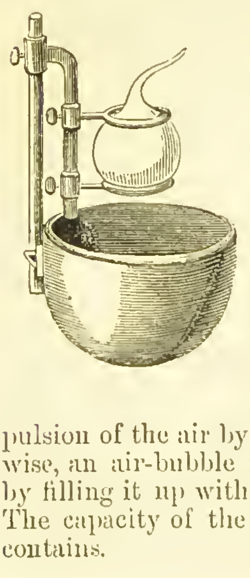


upwards; with a light gas the position would be reversed. When full, the ends of the globe are restopped, and it is again placed upon the balance. Weights will now be required to restore equilibrium, and the calculation can then be made as in the following example:—

Capacity of globe, 235 cc.
Weight of 1 cc. of air at normal temperature and pressure, ·0012937 gram.
Weight of 1 cc. of air at 17° (temperature of room), ·00122 nearly.
Weight of carbon dioxide in globe, ·150 gram.
Weight of air displaced by this 235 cc. of gas, ·286 gram.
Weight of 235 cc. of carbon dioxide, therefore, ·286 + ·150 = ·436.
Density of gas $\frac{·436}{·286} = 1·524$ (air = 1), or $1·524 \times 14·42 = 21·97$ (H = 1). Calculated from formula, 22·0.

VAPOURS.—1. *Dumas' Method.* This method consists in determining the weight of a given volume of the vapour at a known pressure and temperature. A glass globe about 3 inches in diameter, having its neck softened and drawn out in the blowpipe flame, is accurately weighed. About 6 or 7 grams of the volatile liquid are then introduced, by gently warming the globe and dipping the point into the liquid, which is then forced upwards by the pressure of the air as the vessel cools. The globe is heated in a bath of water, oil, or melted paraffin to a temperature from 30° to 50° above the boiling point of the liquid, in order to bring the vapour as nearly as possible into the state in which it obeys the laws of gaseous expansion and contraction by alteration of pressure and temperature. The liquid is then rapidly converted into vapour, which escapes by the narrow orifice, chasing before it the air of the globe. When the issue of vapour has wholly ceased, and the temperature of the bath appears nearly uniform, the open extremity of the point is sealed by a small blowpipe flame. The globe is removed from the bath, suffered to cool, cleansed if necessary, and weighed, after which the neck is broken off beneath the surface of water which has been boiled and cooled out of contact of air. The liquid enters the globe, and, if the expulsion of the air by the vapour has been complete, fills it; if otherwise, an air-bubble is left, whose volume can be easily ascertained by filling it up with water from a burette or other measuring vessel. The capacity of the vessel is determined by weighing the water it contains.

Fig. 19.



From these data the vapour-density (D) may be calculated by means of the formula :

$$D = \frac{P + Vn_t}{(V - v)n'_t}.$$

P = difference of weight (in grams) between the globe filled with air and when filled with vapour.

V = capacity of globe in cubic centimetres.

n_t = weight of one cubic centimetre of air at the temperature at which the globe filled with air was weighed.

n'_t = weight of one cubic centimetre of air at the temperature of sealing the globe.

v is the residual air.

The values of n_t and n'_t (in grams) for every five degrees centigrade from 0° to 300° are given in the Appendix, Table VII.

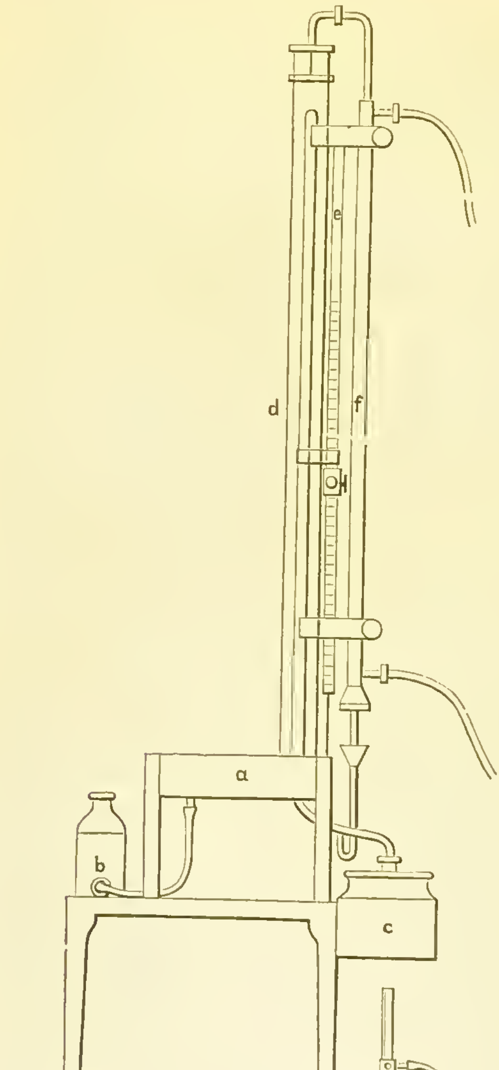
In very exact experiments account must be taken of the change of capacity of the glass globe by the high temperature of the bath. When this correction is neglected, the density of the vapour will come out a little too high. The error of the mercurial thermometer at high temperatures is, however, in the opposite direction.

The preceding method is applicable to the determination of the vapour-densities of all substances whose boiling points are within the range of the mercurial thermometer, that is to say, not exceeding 300° C., and therefore to nearly all volatile organic compounds; indeed, there are but few such compounds which can bear higher temperatures without decomposition. But for mineral substances, such as sulphur, iodine, volatile metallic chlorides, etc., it is often necessary to employ much higher temperatures; and for such cases a modification of the process was devised by Deville and Troost. It consists in using a globe of porcelain instead of glass, heating it in the vapour of a substance whose boiling point is known and constant, and sealing the globe by the flame of the oxy-hydrogen blowpipe. The vapours employed for this purpose are those of mercury, which boils at 350°; of sulphur, which boils at 440°; of cadmium, boiling at 860°; and of zinc, boiling at 1040°. The use of these liquids of constant boiling point obviates the necessity of determining the temperature in each experiment.

2. *Gay-Lussac's Method.*—This method consists in ascertaining the volume occupied by a given weight of a substance when converted into vapour at a known temperature and pressure. It is most readily performed with the apparatus contrived by Hofmann, of which a modification is shown in fig. 20. A glass tube about a metre long and 15 to 20 mm. wide, is filled with mercury and inverted into a small wooden mercurial trough, *a*, whereby a barometric vacuum 20 to 30 mm. high is formed at the top. The long tube is enclosed in another tube, *d*, 30 to 40 mm. wide and 800 to 900 mm. long, connected at the top with a conducting tube of moderate width, which is bent at right angles, and attached to a condenser, *f*, which returns to a copper vessel, *c*, in which water, aniline, or other liquid

can be boiled. The lower part of the wide tube dips into the mercury of the trough in which the barometer-tube stands, and into the space between these two tubes a stream of vapour of water, aniline, or other volatile liquid can be made to pass from the boiler, so as to keep the whole of the barometer-tube at the temperature required for the determination. A reservoir, *b*, of mercury is connected with the trough, and by raising or lowering this the level of the mercury can be regulated. The substance whose vapour-density is to be determined, is introduced into the barometric vacuum in small glass tubes fitted with ground stoppers, which are forced out by the tension of the vapour. The great advantage of this method is that, under the very small pressure to which the enclosed vapour is subjected—which may be reduced to 20 or even 10 millimetres of mercury — the determinations may be made at comparatively low temperatures. Thus, in the case of liquids boiling under the ordinary pressure at 120° or even 150°, the vapour-density may be accurately determined at the temperature of boiling water.

Fig. 20.



By this mode of proceeding, we ascertain the volume which a known weight W′ of substance occupies at a given temperature and pressure; and dividing this by W, the weight of an equal

volume V of air at the same pressure and temperature, which is given by the formula—

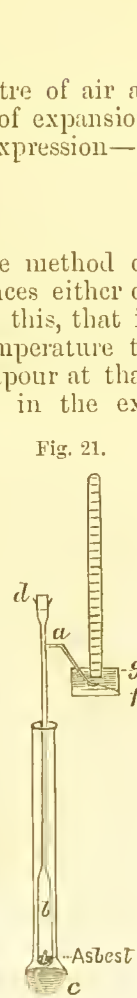
$$W = 0{\cdot}001293\ V \cdot \frac{1}{1 + 0{\cdot}00367\ T} \cdot \frac{P}{760},$$

0·001293 being the weight in grams of a cubic centimetre of air at 0° C. and 760 mm. pressure, and 0·00367 the coefficient of expansion of gases,* we obtain, for the density of the vapour, the expression—

$$D = \frac{W'}{W} = W' \frac{1 + 0{\cdot}00367\ T}{0{\cdot}001293\ V} \cdot \frac{760}{P}.$$

3. *V. and C. Meyer's Method.*—This is a very simple method of determining vapour-densities, and applicable to substances either of low or of high boiling point. Its simplicity consists in this, that it does not require the determination either of the temperature to which the vapour is heated, or of the volume of the vapour at that temperature—both these quantities being eliminated in the expression for the vapour-density—but only of the volume of air displaced by the vapour evolved, this volume being measured at the atmospheric temperature. The apparatus (fig. 21) consists of a cylindrical glass bulb, *b*, having a capacity of about 100 cc., to which is attached by fusion a tube 600 mm. long, terminating in a thimble-shaped enlargement, and having attached to it a side exit-tube *a*, by which the displaced air is transferred to a graduated tube standing in a small water-trough. For substances of boiling point not exceeding 310°, the bulb is heated in a glass tube, which terminates below in a bulb *c* containing various liquids, according to the volatility of the substance under experiment, viz., aniline (b. p. 181·5°), toluidine (202°), ethyl benzoate (212°), amyl benzoate (261°), diphenylamine (310°). The mode of working is as follows :—The bulb, into which a little ignited asbestos has been introduced, is fixed in position in the bath, the end of the exit-tube *a* dipping into the water-trough below the mouth of the graduated tube, which is filled with water and inverted. A cork is now inserted into the top of the vertical tube at *d*, and the extremity of the exit-tube *a* is watched, to see that the temperature in the bulb is uniform. The cork is now taken out, the small tube containing the substance is dropped in, and the cork is quickly replaced. The first few bubbles of air are suffered to escape, but immediately afterwards the inverted tube is placed quickly over the point of the delivery tube *a*. The

Fig. 21.



* The values of the expression $\frac{1}{1 + 0{\cdot}00367\ T}$ have been calculated by C. Greville Williams for all temperatures from 1° to 150° C. (See Table VIII. in the Appendix.)

substance is soon volatilised and displaces air, which issues in a rapid stream into the graduated tube ; and as soon as air ceases to come over, the cork is removed, and the air collected is cooled and measured.

The density of the vapour is calculated by the formula

$$\frac{S \, . \, 760(1 + 0{\cdot}00367t)}{(B - w)V \, . \, 0{\cdot}001293} \text{ or } \frac{S(1 + 0{\cdot}00367t) \, . \, 587780}{(B - w)V},$$

in which S denotes the weight of substance, t the temperature of the water, B the barometric pressure reduced to 0°, w the tension of aqueous vapour, and V the volume of air displaced.

For temperatures above 310°, a bath of molten lead is employed ; and for determining the vapour-densities of inorganic compounds which volatilise only at a red heat or at still higher temperatures, the glass vessel is replaced by one of porcelain or platinum heated in a gas-furnace.

LIQUEFACTION OF GASES.

When water is heated in a boiler the space above the surface of the liquid becomes filled with the vapour of water, which is a clear, transparent substance like common air, becoming visible in the form of cloud only when it escapes into the atmosphere, and is thus chilled, so that a portion of it is converted into minute drops of liquid. The water vapour exerts upon the sides of the boiler a pressure which remains constant after it has reached a maximum, so long as the temperature neither rises nor falls. If now the space occupied by the steam is reduced, or pressure upon the vapour in any way increased, a portion of it will return to the liquid state until the pressure again falls to its former amount ; conversely, if the pressure on the steam is reduced more water will evaporate. Similarly, if the temperature is raised, more vapour is produced and the pressure is increased ; while, if the temperature falls, a portion of the vapour returns to the liquid state. Vapour of water under these circumstances does not comply with the law of Boyle, nor with the law of Gay-Lussac ; it is, therefore, not a gas. But by raising the temperature of a vessel containing water sufficiently high to cause all the water to evaporate, and the resultant vapour to be heated considerably beyond the temperature at which any portion of it can remain liquid, the vapour, without changing in chemical composition, becomes a *gas*. This distinction will be further explained a little later.

The first experiments on the liquefaction of common gases were made, about 1805, by Northmore, who, by the use of a brass condensing syringe and glass receivers, succeeded in liquefying chlorine and probably also sulphur dioxide. But more generally successful experiments in this direction were made by Faraday who, acting upon the idea that gases are merely vapours of very volatile liquids,

succeeded in liquefying eight gases previously regarded as permanent. The subjoined table shows the results of his first investigations with the pressure in atmospheres, and the temperatures at which the condensation takes place.

	Atmospheres.	Temperatures. F.	Temperatures. C.
Sulphur,	2	45°	7·2°
Hydrogen sulphide,	17	50	10
Carbon dioxide,	36	32	0
Chlorine,	4	60	15·5
Nitrogen monoxide,	50	45	7·2
Cyanogen,	3·6	45	7·2
Ammonia,	6·5	50	10
Hydrogen chloride,	40	50	10

The method of proceeding was very simple: the materials were sealed up in a strong narrow tube, together with a little pressure-gauge, consisting of a slender tube closed at one end, and having within it, near the open extremity, a globule of mercury. The gas being disengaged by heat, or by causing the materials to act upon each other, accumulated in the tube, and by its own pressure brought about condensation. The pressure required for this purpose was judged of by the diminution of volume of the air in the gauge.

Fig. 22.

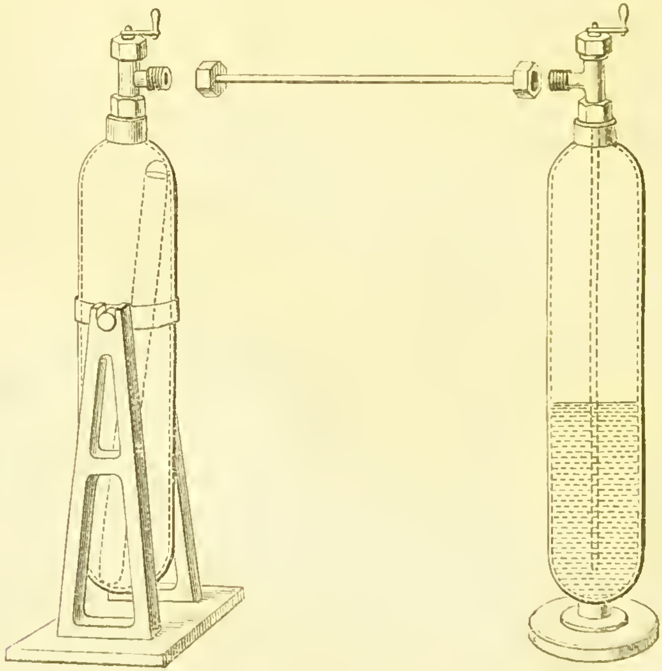
By the use of strong glass tubes, powerful condensing syringes, and a low temperature, produced by means to be presently described, ethylene gas, hydriodic and hydrobromic acids, phosphoretted hydrogen, and the gaseous fluorides of silicon and boron, were successively liquefied. Oxygen, hydrogen, nitrogen, nitric oxide, carbon monoxide, and marsh-gas, refused to liquefy even at -166° F. while subjected to pressures varying from 27 to 58 atmospheres.

Thilorier, of Paris, succeeded in obtaining liquid carbon dioxide in much larger quantity by a similar process. His apparatus (fig. 23) consisted of a pair of strong metallic vessels, one of which served the purpose of a retort, and the other that of a receiver. They were made originally of thick cast-iron, but in consequence of an accident by the bursting of one of these vessels, gun-metal and wrought-iron were subsequently employed. The generating vessel or retort had a pair of trunnions upon which it swung in an iron frame. The joints were secured by collars of lead, and every precaution taken to prevent leakage under the enormous pressure which the vessel has to bear. Bicarbonate of soda and water were placed in the retort together with a copper tube filled with sulphuric acid by which the carbonate was decomposed. The receiver resembled the retort in every respect; it had a similar stop-cock, and was connected with the retort by a strong copper tube and a pair of union screw-

joints ; a tube passed from the stop-cock downwards, and terminated near the bottom of the vessel.

The gas having been generated by mixing the acid with the carbonate in the retort, distillation of the liquid into the receiver was effected by placing the latter in cold water and opening communication between the two vessels.

Fig. 23.



In 1822 it was shown by Cagnard de la Tour that ether, alcohol, and even water when heated in strong glass or steel tubes may be completely converted into gas which occupies a volume no more than about twice the volume of the liquid itself. The pressure exercised in such cases is very great, and Faraday recognised the improbability that increase of pressure, such as any possible apparatus could bear, would be sufficient to reduce this gas again to a liquid. He further perceived that the lowest temperature he had been able to obtain, namely, –166° F., or –110° C., was probably above the temperature at which hydrogen, oxygen, and nitrogen enter into the state corresponding to that of ether in the experiments of de la Tour, and hence that no compression without the conjoint application of a greater degree of cold than had as yet been reached would be sufficient to change these gases to liquids. This prevision was confirmed by the further exact observations published by Andrews in 1869.

Andrews observed that when liquid carbon dioxide is gradually

heated in a sealed tube to 31°, the surface of demarcation between the liquid and gas becomes fainter, loses its curvature, and at last disappears. The space is then occupied by a homogeneous fluid, which exhibits, when the pressure is suddenly diminished, or the temperature slightly raised, a peculiar appearance of moving or flickering striæ throughout its entire mass. At temperatures above 32° no apparent liquefaction of carbon dioxide or separation into two distinct forms of matter can be effected, even under a pressure of 300 or 400 atmospheres. Similar results are obtained with nitrous oxide.

It appears, indeed, that there exists for every liquid a temperature, called by Andrews the "critical point," above which no amount of pressure is sufficient to retain it in the liquid form ; it is therefore not surprising that mere pressure, however intense, should fail to liquefy many bodies which usually exist in the form of gas.

Under the enormous pressures to which gases can be thus subjected without liquefaction, they deviate greatly from the laws of Boyle and Gay-Lussac (pp. 27–29). Andrews found that carbon dioxide at 60·7° under a pressure of 223 atmospheres, is reduced to $\frac{1}{447}$ of its original volume, or to less than one-half the volume it should occupy if it contracted according to Boyle's law. The coefficient of expansion of the same gas by heat increases rapidly with the pressure ; between 6° and 64° it is $1\frac{1}{2}$ times as great under 22 atmospheres, and more than $2\frac{1}{2}$ times as great at 40 atmospheres as at the pressure of 1 atmosphere.

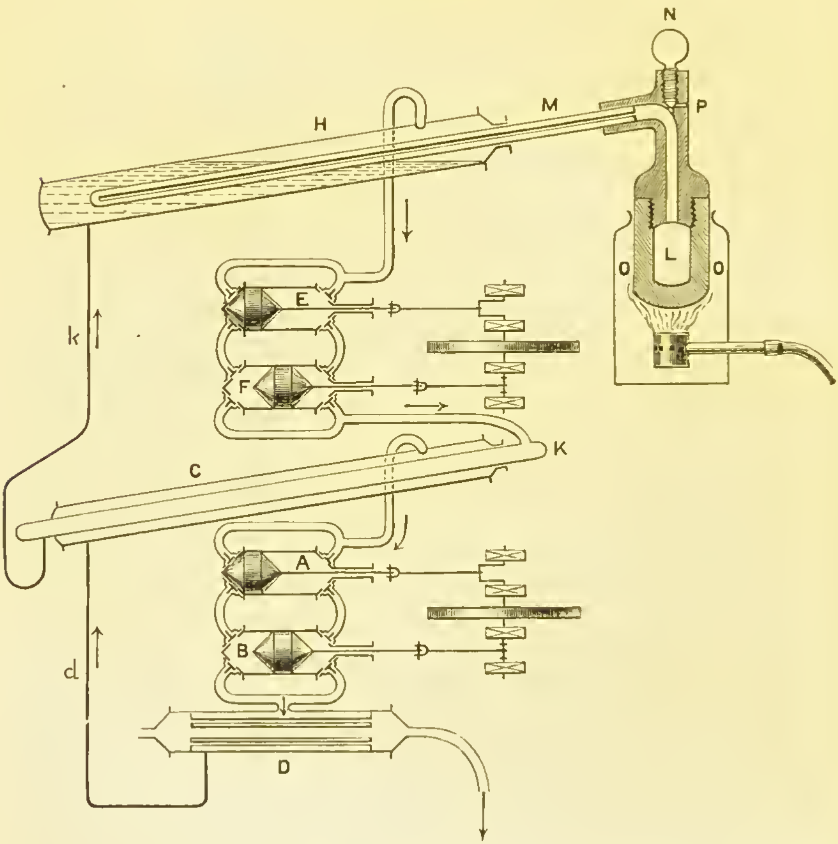
These remarkable observations afford the means of discriminating a gas from a vapour. A body can be said to exist as a gas only when at temperatures above its critical point, and when the pressure is less than the critical pressure, that is the pressure which the substance exerts at its critical point. And recognising the impossibility of liquefying a gas when at temperatures above the critical point, the object of all subsequent experiment has been to cool the gas sufficiently while the pressure is applied. Acting on this principle all the six gases remaining uncondensed by Faraday have now been obtained in the liquid and some even in the solid state. The first step was accomplished at the end of the year 1877 when MM. Cailletet and Pictet almost simultaneously communicated the results of their experiments to the French Academy of Sciences.

Pictet's method was similar in principle to that used by Faraday. In an apparatus of which the essential parts are shown in the accompanying figure 24, oxygen was generated by heating potassium chlorate in a strong wrought-iron bottle, L, to which was attached a copper tube, M, surrounded by a second tube containing liquid carbon dioxide, H, boiling under reduced pressure so as to give a temperature of about – 140° C. The carbon dioxide, as it was drawn away by the pumps, E, F, was cooled by means of liquid sulphur dioxide, contained in a wide tube, C, to about – 65° C., as it is then easily compressed again into the liquid state. A and B represent the pumps by which the evaporated sulphur dioxide is drawn off

and compressed into the receiver D, which is surrounded by cold water.

The apparatus used by Cailletet was constructed upon a different principle. When a gas is compressed heat is given out, and if, when under pressure, it is allowed to expand, heat is absorbed. If this latter operation is carried out under proper conditions, the gas is so chilled that a portion of it may be condensed to the liquid or

Fig. 24.

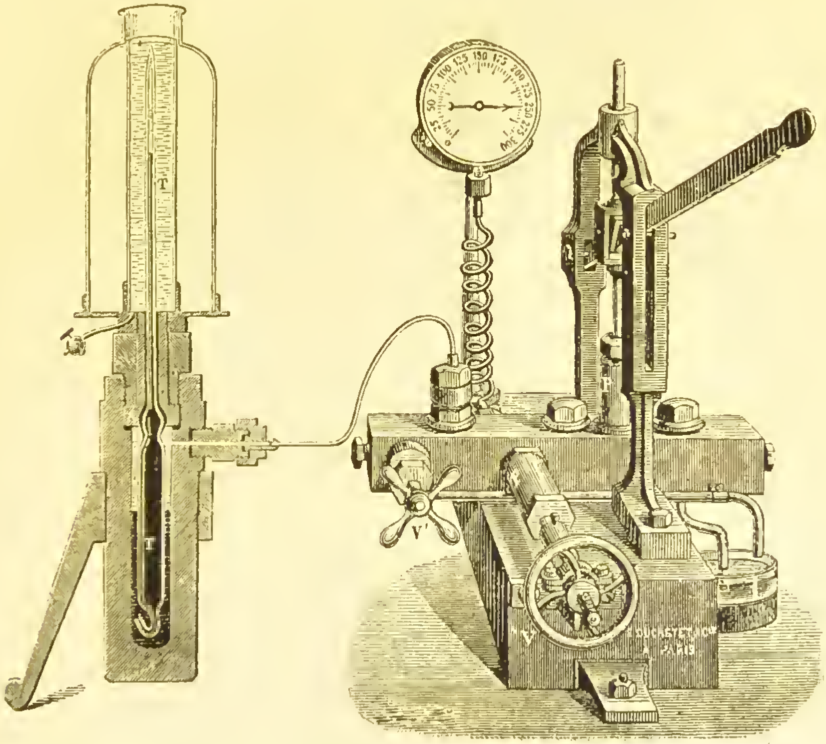


solid state. Cailletet compressed the gas under experiment by means of a hydraulic pump. The gas was contained in a glass reservoir (T, fig. 25), the upper part of which consisted of a narrow thick-walled tube, the lower end being plunged into mercury. The mercury was covered by water which filled the pump, and when the latter was worked, the mercury was driven into the glass vessel, and so compressed the gas to any desired degree. If the tube was filled with oxygen, no visible liquefaction occurred under a pressure of even 300 atmospheres if the temperature was above 119° C., but if the pressure

was suddenly released, a mist appeared which collected in small drops on the sides of the tube. An apparatus slightly modified from the original form, and adapted for lecture demonstration, is shown in the accompanying figure, in which P is the hydraulic pump, P′ a plunger for obtaining higher pressures worked by the wheel V, while the screw V′ gives, when required, the release of pressure.

The use of liquid ethylene as a cooling agent has enabled experimenters to improve upon Pictet's apparatus without altering the

Fig. 25.

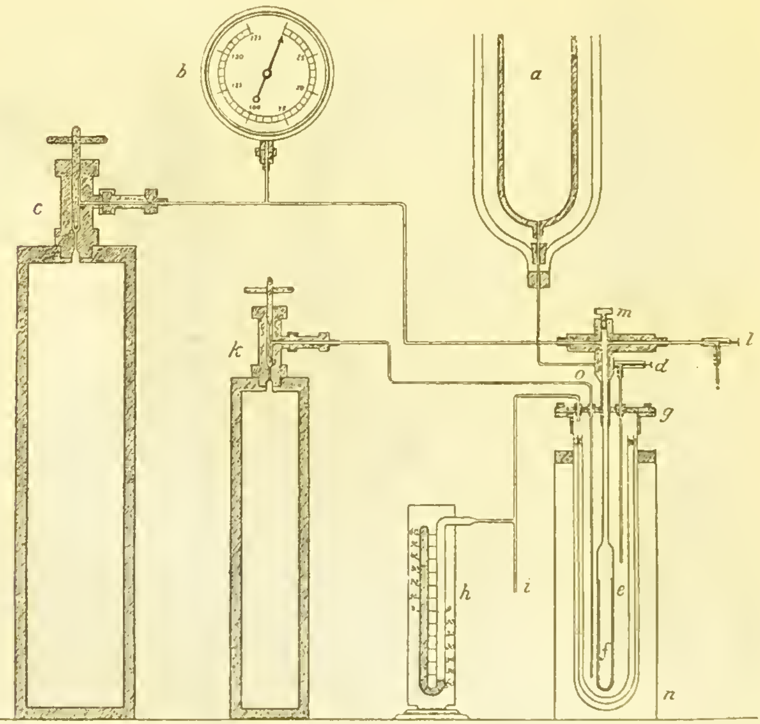


principle. It was with the aid of boiling ethylene that Professor Olszewski first liquefied oxygen in considerable quantity in 1891.

Since that time liquid oxygen and liquid air have been prepared in much larger quantity by Professor Dewar in apparatus of the same type, and liquid oxygen is now regularly employed as a cooling agent, especially in the various attempts which have been made to liquefy hydrogen. The critical temperature of hydrogen has been estimated to be at $-234{\cdot}5°$, consequently it is only possible to effect the liquefaction of this gas by a combination of the principles of Pictet and Cailletet, that is to say the gas must be cooled as much as possible, and further cooled by expansion from pressure. Olszewski states that he obtained evidence of liquefaction of hydrogen in 1884,

by cooling in liquid oxygen, which boils in vacuo at $-211°$, and reducing the pressure on the gas from 190 atmospheres to about 20 atmospheres, its critical pressure. Figure 26 exhibits the arrangement employed by Olszewski for observing the liquefaction of hydrogen and determining its critical temperature and the boiling point of the liquid. The cylinder *a*, of which only the lower part is shown, contains liquid oxygen collected by the combined agency of pressure and cooling by means of liquid ethylene. The glass tube, *f*, is destined for the reception of the liquefied hydrogen: it is

Fig. 26.



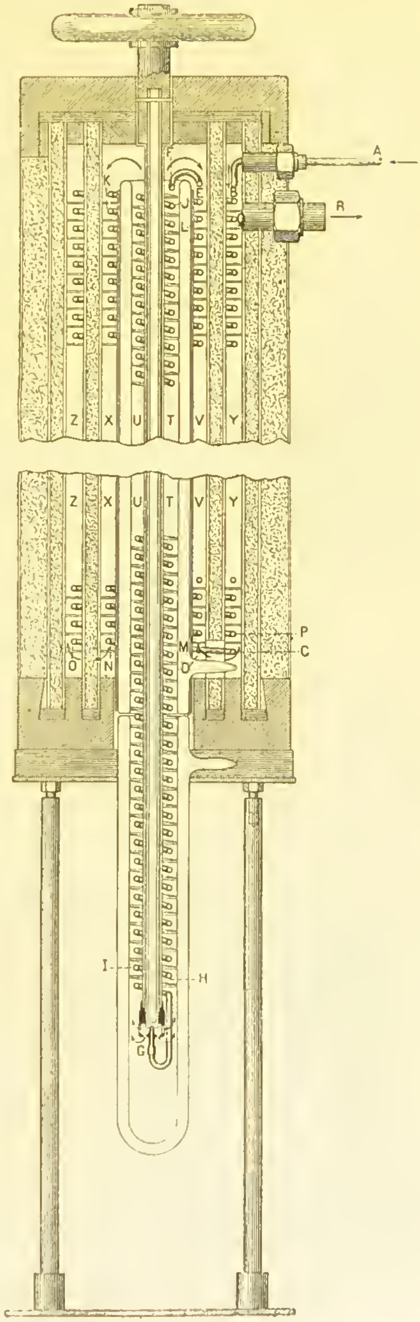
contained within a larger glass tube, *e*, with thin walls and surrounded by two others, closed above by a brass plate, *g*. The top of the tube *f* is connected with the pressure-gauge *b*, and with the iron bottle *c* containing pure and dry hydrogen under a pressure of 150 atmospheres. The cock *l* serves to let the hydrogen out of the tube *f*, thus producing the expansion. Through the upper end of the tube *f*, which is closed by the screw *m*, a thermo-electric junction, or a platinum resistance thermometer, is introduced when the temperature of the hydrogen is to be determined. In order to perform the experiment, the liquid oxygen from *a* is allowed to flow into the tube *e*, and by means of a pump attached to *i*, it is made to boil and

the temperature is reduced to $-211°$. Hydrogen is then admitted into the tube f, at a pressure of 80 atmospheres or more, and by opening l a slow expansion is produced, so that the temperature of the gas sinks below the critical point and a portion of it is liquefied. Liquid hydrogen is said to boil at $-243·5°$ C.

The process of cooling a gas by its own expansion has latterly been applied in a cumulative form to the liquefaction of oxygen and air without the use of a cooling agent, such as liquid carbon dioxide or ethylene. An apparatus, in which this principle is applied, and in which indefinitely large quantities of air can be liquefied, has been constructed by Herr Linde.*

A simple form of apparatus, suitable for laboratory purposes where only small quantities of liquid are required, has been devised by Dr W. Hampson. In this case, as in the larger apparatus of Linde, the compressed gas passes through concentric coils A, B, C, D, E, F (fig. 27) round which circulates the cold expanded air after escape from a narrow orifice G of peculiar construction. The gas, as it liquefies, is collected in a double-walled glass tube H.I., of which the space between the walls has been rendered vacuous and thus non-conducting. The use of vacuum vessels for this purpose was introduced by Professor Dewar. Hampson's apparatus has been modified by Mr Lennox, so as to

Fig. 27.



* A description of this apparatus will be found in *The Engineer*, October 4, 1895.

economise the compressed air or other gas which it is desired to liquefy. In this form of apparatus the coils are first cooled to about –80°, by passing liquid carbon dioxide into alcohol contained in the case which surrounds the coil, and by the addition of this device, oxygen released from a pressure of about 120 atmospheres may be collected in a liquid form in a few minutes.

In the following table are given the physical characters of the six gases formerly described as permanent gases :—

Name.	Critical Temperature.	Critical Pressure. — Atmospheres.	Boiling Point under Atmospheric Pressure.	Freezing Point.
	°		°	°
Hydrogen, . .	–234·5	20	–243·5	?
Nitrogen, . .	–146·0	35	–194·4	–214·0
Carbonic Oxide, .	–139·5	35·5	–190·0	–207·0
Oxygen, . .	–118·8	50·8	–182·7	?
Nitric Oxide, .	–93·5	71·2	–153·6	–167·0
Methane, . .	–81·8	54·9	–164·0	–185·8

COMBUSTION.

When any solid substance capable of bearing the fire is heated to a certain point, it emits light, the character of which depends upon the temperature. Thus a bar of platinum or a piece of porcelain, raised to a particular temperature, becomes what is called red-hot, or emissive of red light; at a higher degree of heat, this light becomes whiter and more intense, and when urged to the utmost, as in the case of a piece of lime placed in the flame of the oxy-hydrogen blow-pipe, the light becomes exceedingly powerful, and acquires a tint of violet. Bodies in these states are said to be *incandescent* or *ignited*.

If now the same experiment be made on a piece of charcoal, similar effects will be observed; but something in addition, for whereas the platinum and porcelain, when removed from the fire, or the lime from the blow-pipe flame, immediately begin to cool, and emit less and less light, until they become quite dark, the charcoal maintains to a great extent its high temperature. Unlike the other bodies, too, which suffer no change whatever, either of weight or substance, the charcoal gradually wastes away until it disappears. This is what is called *combustion*, in contradistinction to mere ignition; the charcoal burns, and its temperature is kept up by the heat evolved in the act of union with the oxygen of the air.

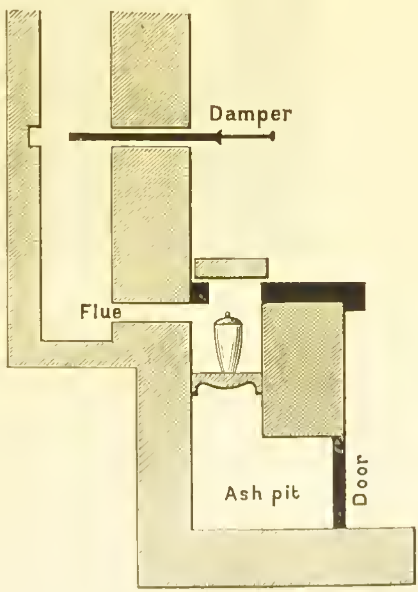
In the most general sense, a body in a state of combustion is one in the act of undergoing intense chemical action: any chemical

action whatsoever, if its energy rise sufficiently high, may produce the phenomenon of combustion, by *heating the body to such an extent that it becomes luminous.*

In all ordinary cases of combustion, the action lies between the burning body and the oxygen of the air; and since the materials employed for the economical production of heat and light consist of carbon chiefly, or that substance conjoined with a certain proportion of hydrogen and oxygen, all common effects of this nature are cases of the rapid and violent oxidation of carbon and hydrogen by the aid of the free oxygen of the air. The heat is due to the act of chemical union, and the light to the elevated temperature.

By this principle, it is easy to understand the means which must be adopted to increase the heat of ordinary fires to the point necessary to melt refractory metals, and to bring about certain desired effects of chemical decomposition. If the rate of consumption of the fuel can be increased by a more rapid introduction of air into the burning mass, the intensity of the heat will of necessity rise in the same ratio, the quantity of heat evolved being fixed and definite for the same constant quantity of chemical action. This increased supply of air may be effected by two distinct methods: it may be forced into the fire by bellows or blowing-machines, as in the common forge and in the blast and cupola furnaces of the iron-worker; or it may be drawn through the burning materials by the help of a tall chimney, the fireplace being closed on all sides, and no entrance of air allowed, save between the bars of the grate. Such is the kind of furnace generally employed by the scientific chemist in assaying and in the reduction of metallic oxides by charcoal: the principle will at once be understood by the aid of the sectional drawing (fig. 28), in which a crucible is represented arranged in the fire for an operation of the kind mentioned. The furnace is, of course, lined with refractory fire-bricks, the top consists of a slab of cast-iron and the furnace mouth, at the top, is closed by fire-brick tiles bound with iron.

Fig. 28.

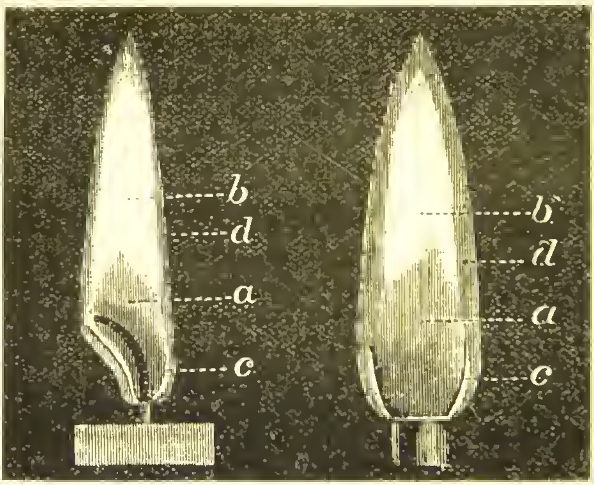


The "reverberatory" furnace (for illustrations, *see* Lead and Copper) is one very much used in the arts when substances are to be exposed to heat without contact with the solid fuel. The fire-chamber

is separated from the bed or hearth of the furnace by a wall or *bridge* of brickwork, and the flame and heated air are reflected downwards by the arched form of the roof. Any degree of heat can be obtained in a furnace of this kind—from the temperature of dull redness to that required to melt very large quantities of cast-iron. The fire is urged by a chimney provided with a sliding-plate or damper to regulate the draught.

Structure of Flames.—The flames of hydrogen, of coal gas, and of a candle or oil lamp burning in the air present very different appearances but they agree in being hollow, the chemical action between the atmospheric oxygen and the gases of the flame being confined to the base of the flame, and a region which may be defined as a hollow cone rising from the base. A candle flame consists of four parts easily distinguished by the eye. In fig. 29 a candle flame

Fig. 29.



is compared with a flame of the same size of coal gas issuing from a tube, and it can at once be seen that they correspond to each other in the distribution of the several parts. At the base (*c*) is a bright blue region which gradually shades off into a thin scarcely luminous mantle (*d*) which sheathes the entire flame. A dark space occupies the lower central portion, (*a*), of each, and this is surmounted by the bright yellow luminous portion (*b*). The only essential difference between a candle flame and a gas flame is the fact that in the latter the combustible gas issues ready made into the bottom of the cone of combustion, while in the former the wick draws up the melted fat which is then converted into gas by the heat of the flame itself.

If the gas in either flame is mingled with air, as happens when exposed to the wind or if air be blown into the flame through a tube, the illuminating power disappears almost entirely, and the whole

flame presents the colour usually visible only at the base. In this condition it no longer deposits soot upon a cold surface brought into contact with the flame. Advantage is taken of this fact in the construction of various so-called air-burners commonly in use, not only in the laboratory, but for cooking and various domestic and manufacturing purposes. These are nearly all modifications of the burner devised more than thirty years ago by Bunsen, and invariably known as the Bunsen burner. The apparatus consists of a chamber *a*, at the bottom of which is a small aperture through which the gas issues from the supply-pipe *t*, under slight pressure. The sides of this chamber, usually made of solid iron or brass, have several holes for the admission of atmospheric air, and at the top is inserted a vertical brass tube, immediately over the small hole from which the gas escapes. The latter, issuing with some force, expands into a jet, and draws up with it the air which enters by the side holes; and on lighting the gaseous mixture which escapes at the top of the tube, it burns with a pale, smokeless flame, of peculiar structure and greenish-blue light. The amount of air admitted can be regulated by opening or closing the holes in the base of the burner. The flame should burn quietly, at the same time without any appearance of yellow light. If it roars, this is a sign that there is an excess of air; if luminous, it shows that the air is deficient, and this may happen either from the closure of one or more of the air holes at the base, or from the fact that the aperture by which the gas escapes into the tube is too large, and, consequently, that the gas does not draw in with it sufficient air for complete combustion. The flame of the Bunsen burner is shown diagrammatically in figure 31. On examination of such a flame, it will be seen at once that it is made up of two cones, of which the inner is more sharply defined than the outer. At *a* is a space which is filled with a cold mixture of gas with an amount of air insufficient for its complete combustion. That the gas at this point is cool, may be demonstrated by thrusting into it the head of a common match. The wood passing through the shell of flame will be charred, but the head will not be ignited unless it is raised to the tip of the cone *b*, or drawn aside into the space between the inner and outer cones.

Fig. 30.

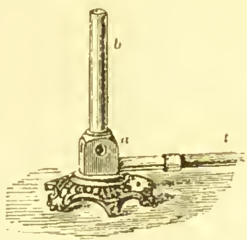
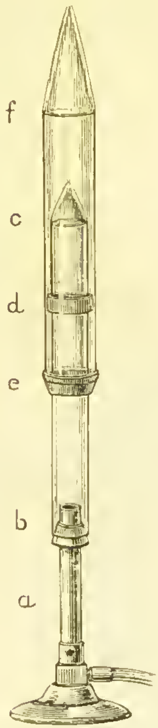


Fig. 31.

The double structure of the Bunsen flame and the nature of the gases between the two cones have been considerably elucidated by a beautiful experiment devised by Professor Smithells. The apparatus is represented in figure 32. A long glass tube *b* is fixed upon a Bunsen burner *a*, so as

practically to form an extension of the brass tube, and the usual non-luminous flame may be obtained at the top. Upon reducing the supply of gas or increasing the amount of air, the inner cone becomes shorter and greenish in colour, and by carefully regulating the gas supply the flame will recede slowly down the tube, at the same time becoming divided into two separate cones, the one bright green at a varying height within the tube, the other pale, scarcely visible, remaining at the top. If now a second wider tube *c* be adapted to the first, by a rubber joint *e* and a ring of asbestos *d*, as shown in the figure, it will be easy so to adjust the gas supply that the inner cone will separate from the outer, descend the tube, and sit permanently upon the mouth of the inner glass tube *b*. The space between the two cones will then be filled with the products of the combustion taking place in the inner cone, together with atmospheric nitrogen. These products include not only carbon dioxide and water vapour, but relatively large quantities of carbon monoxide and hydrogen. When coal gas is burning at a Bunsen burner under ordinary conditions, the volume of air mixing with the gas in the tube is about $2\frac{1}{2}$ times its volume, but the mixture burning at the inner tube of Smithells' burner contains about 4·8 volumes of air to 1 volume of gas. This is an amount which approaches the proportion required for complete combustion of all the combustible ingredients of the gas, and such a mixture is explosible. If a tube were filled with such a mixture at rest, the flame would travel along the tube with a certain velocity, but when the gaseous mixture is moving in the opposite direction, with a velocity exactly equal to the rate of inflammation, the cone of flame remains stationary within the tube. If, however, the flame is capable of being propagated down the tube faster than the ascending current of gas, then the flame will descend as seen in a Bunsen burner when the gas is turned too low or too much air is admitted, and the flame strikes down with a sound of explosion to the bottom of the tube.

Fig. 32.



Luminosity of Flame.—Davy, in 1818, enunciated the theory that the luminosity of the flames of candles and oil is due to "the decomposition of part of the gas towards the interior of the flame, where the air is in smallest quantity, and the deposition of *solid charcoal*, which, first by *ignition* and then by its *combustion*, increases in a high degree the intensity of the light."

The explanation formerly given of this decomposition of the gas in such a flame was based upon the assumption that, when a compound

of carbon and hydrogen was ignited in the presence of an amount of oxygen insufficient to oxidise both completely, the hydrogen was burned first to water, leaving more or less of the carbon in the solid state, which, becoming heated to a high temperature by the burning hydrogen, gave out light. Early in the present century, however, Dalton had observed that when ethylene, C_2H_4, is fired with an equal bulk of oxygen, the gaseous products include carbonic oxide and unburnt hydrogen; and more recent experiments of the same kind have proved that, when burnt with less than its own bulk of oxygen, ethylene yields also appreciable quantities of methane, CH_4, and dense hydro-carbons, among which acetylene, C_2H_2, is prominent.

It is therefore certain that the preferential combustion of the hydrogen cannot be the cause of the liberation of carbon in the midst of a flame, though it is now very generally admitted that the light of a common flame is due to the ignition of a cloud of minute solid carbon particles. The *structure* of the flame of burning methyl alcohol, or common spirit of wine, appears to be the same as that of the candle and of common gas already described; but these flames emit practically no yellow light. Compounds of this kind containing a relatively small proportion of carbon give but little light. It is only compounds such as those contained in paraffin or sperm oil which are capable of yielding a highly luminous flame, and the light emitted is in all cases considerably increased by increasing the temperature. Marsh gas, for example, burns under ordinary circumstances with a flame which gives very little light; but if it be first heated by passing through a red-hot tube, its luminosity will be greatly increased.

That a luminous hydro-carbon flame holds solid particles in suspension appears to be proved by the fact that when an image of a flame standing in the track of the beam from an electric arc is cast upon a screen, the image is seen to be partially opaque in the part of the flame which is most luminous; also that when a beam of sunlight is thrown, by means of a lens, across a flame, two patches of light are seen on either side of the cone formed by the flame, such as would be produced by letting the solar ray fall upon a cloud of dust or of smoke. The question as to the origin of this deposited cloud of solid carbon has not been completely answered. There seems to be a general belief that it is due to the action of heat upon gaseous hydro-carbons within the cone of combustion, but there is much difference of opinion as to the chemical nature of the change. On the one hand it might result from the splitting up of ethylene into methane and carbon,

$$C_2H_4 = CH_4 + C.$$

Or since acetylene is always present in the interior of such flames, and it is an endothermic (see later in the book) compound, its decomposition has been supposed to be the source of the deposited carbon.

The solid particle theory was supported by Davy by experiments showing that the introduction of solid matter, even though incom-

bustible, into a non-luminous flame of burning hydrogen or spirit of wine, made it give out light. Thus, powdered magnesia, lime, or dust of any kind, thrown into such a flame, causes luminescence, and at the present time advantage is taken of the property of glowing brightly when heated, possessed by many solid earths, in the production of the so called "incandescent" gas burners now common everywhere. Another example of the utilisation of this property is seen in the "lime-light," used at theatres and for the projection of pictures upon a screen. In this case a jet of mixed oxygen and hydrogen, or more commonly of oxygen blown through a flame of coal gas, is directed upon the side of a cylinder of compressed lime. The latter becoming heated to a high temperature emits a dazzling white light. The brilliant light emitted by burning magnesium is also chiefly due to the incandescence of the solid particles of magnesia resulting from the oxidation of the metal.

It is possible, however, as pointed out by Dr Frankland, to produce very bright flames in which no solid particles are present. Metallic arsenic burnt in a stream of oxygen produces an intense white flame, although both the metal itself and the product of its combustion (arsenious oxide) are gaseous at the temperature of the flame. The combustion of a mixture of nitric oxide and carbon bisulphide also produces a dazzling white flame, without any separation of solid matter.

The conditions most essential to luminosity in a flame are a high temperature, and the presence of gases or vapours of considerable density. The effect of high temperature is seen in the greater brightness of the flame of sulphur, phosphorus, and indeed all substances, when burnt in pure oxygen, as compared with that which results from their combustion in common air; in the former case the whole of the substances present take part in the combustion, and generate heat, whereas in the latter the temperature is lowered by the presence of a large quantity of nitrogen, which contributes nothing to the effect. The relation between the luminosity of a flame and the vapour-densities of its constituents may be seen from the following table, in which the vapour-densities are referred to that of hydrogen as unity.

Relative Densities of Gases and Vapours.

Hydrogen,	1	Arsenious chloride,	90¾
Water,	9	Phosphoric oxide,	142
Hydrogen chloride,	18¼	Metallic arsenic,	150
Carbon dioxide,	22	Arsenious oxide,	198
Sulphur dioxide,	32		

A comparison of these numbers shows that the brightest flames are those which contain the densest vapours. Hydrogen burning in chlorine produces a vapour more than twice as heavy as that resulting from its combustion in oxygen, and accordingly the light produced in the former case is stronger than in the latter; carbon and

sulphur burning in oxygen produce vapours of still greater density, namely, carbon dioxide and sulphur dioxide, and their combustion gives a still brighter light; lastly, phosphorus, which has a very dense vapour, and likewise yields a product of great vapour-density, burns in oxygen with a brilliancy which the eye can scarcely endure. Moreover, the luminosity of a flame is increased by condensing the surrounding gaseous atmosphere, and diminished by rarefying it. The flame of arsenic burning in oxygen may be rendered quite feeble by rarefying the oxygen; and, on the contrary, the faint flame of an ordinary spirit-lamp becomes very bright when placed under the receiver of a condensing-pump. Frankland had also found that candles give much less light when burning on the top of Mont Blanc than in the valley below, although the rate of combustion in the two cases is nearly the same. The effect of condensation in increasing the brightness of a flame is also strikingly seen in the combustion of a mixture of oxygen and hydrogen, which gives but a feeble light when burnt under the ordinary atmospheric pressure, as in the oxy-hydrogen blow-pipe, but a very bright flash when exploded in the Cavendish eudiometer (fig. 38), in which the water-vapour produced by the combustion is prevented from expanding.

Temperatures of Ignition.—The Safety Lamp.—The *kindling-point*, or temperature at which combustion commences, is very different with different substances; phosphorus will sometimes take fire in the hand; sulphur requires a temperature exceeding that of boiling water; charcoal must be heated to redness. Among gaseous bodies similar differences are observed; hydrogen is inflamed by a red-hot wire; light carburetted hydrogen requires a white heat to kindle it. When flame is cooled by any means below the temperature at which the rapid oxidation of the combustible gas occurs, it is at once extinguished. Upon this depends the principle of Sir Humphrey Davy's *Safety-Lamp*.

Light carburetted hydrogen, or marsh-gas, is frequently disengaged in large quantities in coal mines, and forms the chief ingredient in the gas known as *fire-damp*. This gas, mixed with seven or eight times its volume of atmospheric air, becomes highly explosive, taking fire at a light and burning with a pale-blue flame; and many fearful accidents have occurred from the ignition of large quantities of mixed gas and air occupying the extensive galleries and workings of a mine. Davy undertook an investigation with a view to discover some remedy for this constantly occurring calamity; and his labours resulted in some exceedingly important discoveries respecting flame, which led to the construction of the lamp which bears his name.

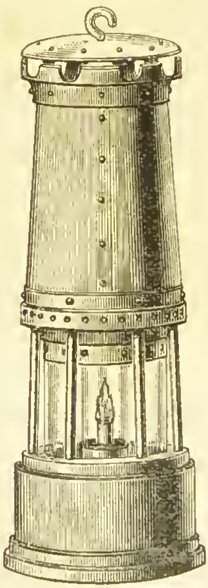
When two vessels filled with a gaseous explosive mixture are connected by a narrow tube, and the contents of one are fired by the electric spark, or otherwise, the flame is not communicated to the other, provided the diameter of the tube, its length, and the conducting power for heat of its material, bear a certain proportion to each other; the flame is extinguished by cooling, and its transmission rendered impossible.

In this experiment, high conducting power and diminished diameter compensate for diminution in length; and to such an extent can this be carried, that metallic gauze, which may be looked upon as a series of very short square tubes arranged side by side, when of sufficient degree of fineness, arrests in the most complete manner the passage of flame in explosive mixtures.

The miner's safety-lamp is merely an ordinary oil-lamp, the flame of which is enclosed in a cage of wire gauze, made double at the upper part, and containing about 400 apertures to the square inch. The tube for supplying oil to the reservoir reaches nearly to the bottom of the latter, while the wick admits of being trimmed by a bent wire passing with friction through a small tube in the body of the lamp; the flame can thus be kept burning for any length of time, without the necessity of unscrewing the cage.

In modern safety-lamps (fig. 33) the flame is usually surrounded by a glass cylinder, which permits the passage of a larger amount of light, and protects the flame from the effects of strong currents of air by which it might be carried through the gauze. The upper part is constructed of wire gauze, as in Davy's lamp, and usually enclosed in sheet metal. When this lamp is taken into an explosive atmosphere, although the fire-damp may burn within the cage with such energy as to heat the metallic tissue to dull redness, the flame is not communicated to the mixture on the outside.

Fig. 33.



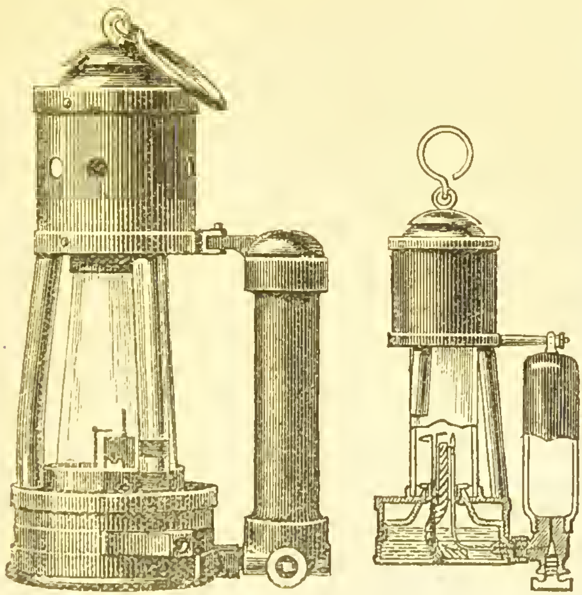
These effects may be studied by suspending the lamp in a large glass jar, and gradually admitting coal-gas below. The oil-flame is at first elongated, and then, as the proportion of gas increases, extinguished, while the interior of the gauze cylinder becomes filled with the burning mixture of gas and air. As the atmosphere becomes pure, the wick is once more relighted. When small proportions of inflammable gas are present a pale blue "cap" appears over the flame of the lamp, and by its height and appearance the miner is able to measure roughly the amount of gas in the atmosphere of a pit.

A safety lamp has been devised by Professor Clowes, expressly for the purpose of testing the air of coal mines or other places where inflammable gas may accumulate. This is a lamp of modern form, supplied with the means of obtaining a small hydrogen flame in place of the ordinary luminous flame. The lamp is shown in fig. 34, from which it will be seen that a small steel cylinder which contains compressed hydrogen gas is attached to the lamp. When a test is to be made the luminous flame would be gradually reduced in size by drawing down the wick, when, if a distinct cap is observed, the

amount of gas will be between 3 and 6 per cent. If no cap is seen over the oil-flame, the hydrogen is turned on and a small hydrogen flame of the standard height of 10 mm. is lighted and a cap is looked for over the flame. As little as 0·25 per cent. of fire-damp can be thus detected.

Slow Combustion.—Phosphorus exposed to the air at common temperatures in a dark room exhibits light and gives off fumes which are also luminous. This luminosity is apparently due to the slow combustion of the phosphorus, attended by the production of a mixture of its oxides. If common ether is sprinkled upon a hot iron plate in a dark room, the vapour which rises undergoes partial oxidation, at the same time producing luminous clouds, but no flame of the ordinary kind. Oxygen and hydrogen may be kept mixed at common temperatures for any length of time without combination

Fig. 34.



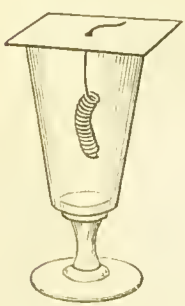
taking place, but, under particular circumstances, they unite quietly and without explosion. Many years ago, Döbereiner discovered that finely divided platinum possesses the power of determining the union of the gases; and, subsequently, Faraday showed that the state of minute division is by no means indispensable, since rolled plates of the metal have the same property, provided their surfaces are absolutely clean. Neither is the effect strictly confined to platinum; other metals, as palladium and gold, and even stones and glass, exhibit the same property, although in a far lower degree, since they often require to be aided by a little heat. When

a piece of platinum foil, which has been cleaned by hot oil of vitriol and thorough washing with distilled water, is thrust into a jar containing a mixture of oxygen and hydrogen standing over water, combination of the two gases immediately begins, and the level of the water rapidly rises, whilst the platinum becomes so hot that drops of water accidentally falling upon it enter into ebullition. If the metal be very thin and quite clean, and the gases pure, its temperature rises after a time to actual redness, and the residue of the mixture explodes. But this is an effect altogether accidental, and dependent upon the high temperature of the platinum, which high temperature has been produced by the preceding quiet combination of the two bodies. When the platinum is reduced to a state of minute division, and its surface thereby much extended, it becomes immediately red-hot in a mixture of hydrogen and oxygen, or hydrogen and air ; a jet of hydrogen thrown upon a little of the spongy metal, contained in a glass or capsule, is at once kindled, and on this principle machines for the production of instantaneous light have been constructed. These, however, act well only when constantly used ; the spongy platinum is apt to become damp by absorption of moisture from the air, and its power is then for the time lost.

The best explanation that can be given of these curious effects is to suppose that solid bodies in general have, to a greater or less extent, the property of condensing gases upon their surfaces (as shown p. 33), and that this faculty is exhibited pre-eminently by certain of the non-oxidisable metals, as platinum and gold. Oxygen and hydrogen may thus, under these circumstances, be brought, as it were, within the sphere of their mutual attractions by a temporary increase of density, whereupon combination ensues. Coal-gas and ether or alcohol vapour may also be made to exhibit the phenomenon of quiet oxidation under the influence of this remarkable surface-action.

Experiments.—1. A close spiral of slender platinum wire, a roll of thin foil, or even a common platinum crucible, heated to dull redness, and then held in a jet of coal-gas, becomes strongly ignited, and remains in that state as long as the supply of mixed gas and air is kept up, the temperature being maintained by the heat disengaged in the act of union. Sometimes the metal becomes white-hot, and then the gas takes fire.

Fig. 35.



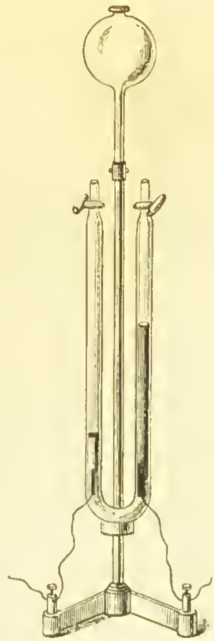
2. If such a coil of wire be attached to a card, and suspended in a glass containing a few drops of ether, having previously been made red-hot in the flame of a spirit-lamp, it will continue to glow until the oxygen of the air is exhausted, giving rise to the production of an irritating vapour which attacks the eyes. The combustion of the ether is in this case but partial ; a portion of its hydrogen is alone removed, and the whole of the carbon left untouched. A similar effect may be observed by suspending a coil of thin platinum wire over the wick of a spirit-lamp.

Oxides of Hydrogen.

There are two oxides of hydrogen—namely, the monoxide, which is water, and the dioxide, discovered in the year 1818 by Thénard.

Water.—It appears that the composition of water was first demonstrated in the year 1781 by Cavendish ; but the discovery of the exact proportions in which oxygen and hydrogen unite in generating that most important compound has, from time to time to the present day, occupied the attention of some of the most distinguished cultivators of chemical science. There are two distinct methods of research in chemistry—the *analytical*, or that in which the compound is resolved into its elements, and the *synthetical*, in which the elements are made to unite and produce the compound. The first method is of much more general application than the second ; but in this particular instance both may be employed, although the results of the synthesis are the more valuable.

Fig. 36.



When a current of electricity is passed through water mixed with a small quantity of any mineral acid, oxygen gas is evolved from the pole or plate connected with the copper, platinum, or carbon of the battery, and hydrogen gas is disengaged from the pole connected with the zinc of the battery, no visible change occurs in the intermediate liquid. The gases can be collected and measured. A convenient form of apparatus is shown figure 36, in which the wires are supposed to connect the platinum plates within the tubes with a battery of any convenient form.

When this experiment has been continued for a sufficient time, it will be found that the volume of the hydrogen is twice that of the oxygen. If the gases are collected at the beginning of the experiment, the proportion of oxygen is slightly less than half the measure of the hydrogen, partly owing to the greater solubility of oxygen in water, partly owing to the production of a little hydrogen peroxide.

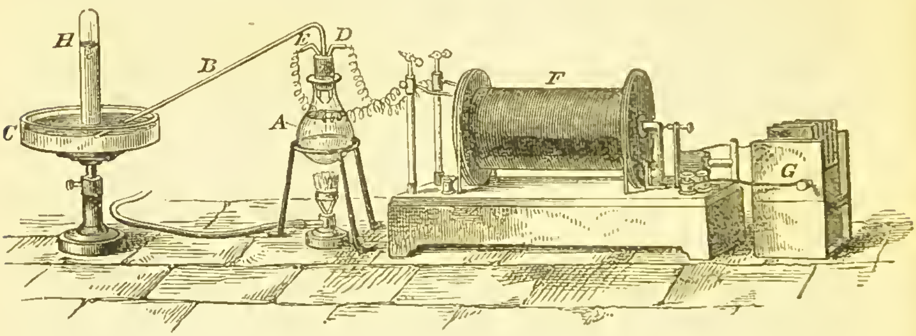
Water is likewise decomposed into its constituents by heat. This effect may be produced by passing sparks from an induction coil F through steam evolved from water kept boiling in a flask A fitted with a tube for conveying the gases into a tube H, as shown in fig. 37. The two gases are obtained in very small quantities at a time.

When oxygen and hydrogen, both as pure as possible, are mixed in the proportions mentioned, passed into a strong glass tube standing over mercury, and exploded by the electric spark, all the mixture

disappears, and the mercury is forced up into the tube, filling it completely.* The same experiment may be made with the explosion vessel usually called Cavendish's eudiometer (fig. 38). The instrument is exhausted at the air-pump, and then filled from a capped jar with the mixed gases; on passing an electric spark by the wires shown at *a*, explosion ensues, and the glass becomes bedewed with moisture; and if the stop-cock be then opened under water, the latter will rush in and fill the vessel, leaving merely a bubble of air, the result of imperfect exhaustion.

But the process upon which most reliance is placed for demonstrating the composition of water, is that in which pure copper oxide is reduced at a red heat by hydrogen, and the water so formed is collected and weighed. This oxide suffers no change by heat alone, but contact with hydrogen, or any common combustible matter, at a

Fig 37.



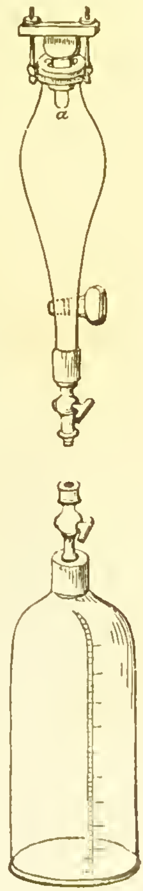
high temperature, suffices to reduce a corresponding portion to the metallic state.

By the use of this method the proportions of oxygen and hydrogen contained in water were first determined with an approach to accuracy by Dumas in 1842. The principle is simple enough in itself, but its application is attended by many difficulties. The hydrogen must be not only pure but perfectly dry; the apparatus must be entirely free from air, a point of great importance, but very difficult to secure, inasmuch as air and other gases adhere strongly to the surface of all solids, glass included. The apparatus employed by Dumas is represented in figure 39. The hydrogen generated from zinc and sulphuric acid in F passes through a solution of lead nitrate to arrest sulphuretted hydrogen; through silver sulphate to remove arsenetted hydrogen; and through caustic potash to absorb traces of acid. Lastly, it must be dried by passage through several tubes filled with glass steeped in strong sulphuric acid and with phosphoric anhydride. The oxide of copper is contained in a globe with two

* Recent very careful determinations make the combining proportions of hydrogen and oxygen as 2·00285 to 1 by volume at 0°. A. Scott, *Phil. Trans.*, 1893.

necks B, and provided with two stop-cocks. After being strongly heated in a current of air with the object of removing every trace of moisture, the globe is allowed to cool, the air is removed by the air-pump, and after closing the taps, the globe with the copper oxide in it is weighed. The bulb in which the water, B′, is to be collected is connected with several tubes containing sulphuric acid and phosphoric oxide, so that every trace of water vapour that might be carried away shall be arrested. The whole of this part of the apparatus is weighed. The several parts of the apparatus are united together by air-tight joints, and a current of hydrogen is caused to traverse the entire apparatus during several hours before heat is applied to the oxide of copper. When the air has been completely expelled the oxide of copper is heated to redness by the lamp, and when the greater part has been reduced to metallic copper, the globe is allowed to cool, exhausted again, and weighed. Its loss of weight represents the oxygen which has been removed. The difference between the weight of the water found and that of the oxygen is, of course, the weight of the hydrogen. The results of many experiments made in this manner led to the conclusion that the ratio of the oxygen to the hydrogen in water is not exactly 8 to 1 or 16 to 2, but is more correctly expressed as 15·96 to 2. The composition of water inferred more recently from the determinations of the relative densities of oxygen and hydrogen, made by Lord Rayleigh, and the proportions by volume in which they combine according to Mr Scott (*loc. cit.*), lead to a still lower value for the atomic weight of oxygen, viz., 15·8 approximately.

Fig. 38.

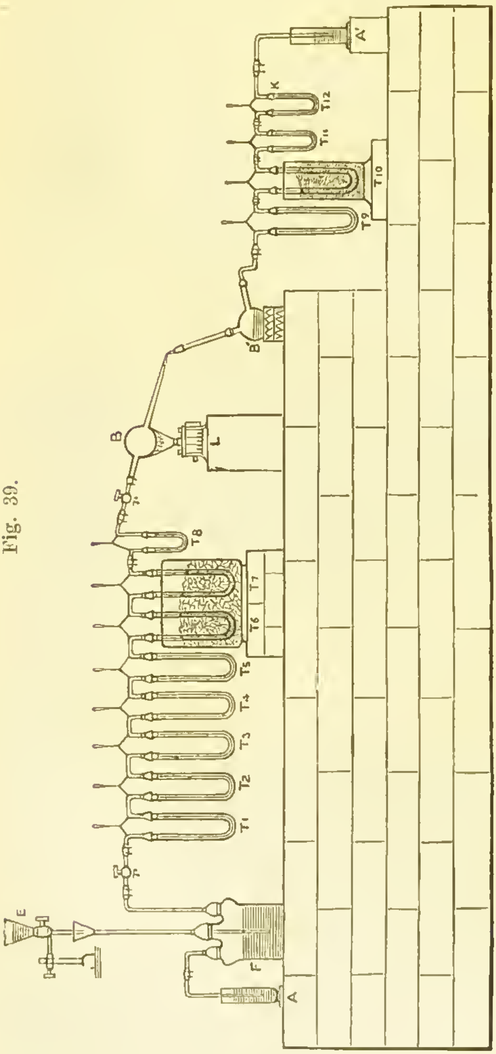


The relative density of steam or vapour of water is found by experiment to be 0·624, compared with air at the same temperature and pressure, or 9 as compared with hydrogen. Now, it has been already shown that water is composed of two volumes of hydrogen and one volume of oxygen; and if the weight of one volume of hydrogen be taken as unity, that of two volumes hydrogen (= 2) and one volume oxygen (= 16) will together make 18, which is the weight of two volumes of water-vapour. Consequently *water in the state of vapour consists of two volumes of hydrogen and one volume of oxygen condensed into two volumes.* The best method of demonstrating this important fact by direct experiment was devised by Hofmann. It consists in exploding a mixture of two volumes of hydrogen and one volume of oxygen by the electric spark in a eudiometer tube, which is kept at or a little above the temperature of boiling water, so that the water produced by the combination of the gases remains in the state of vapour instead of at once condensing to the liquid form. It

is then seen that the three volumes of mixed gas are reduced after the explosion to two volumes.

The experiment is conducted in the following manner. The U-shaped eudiometer represented in fig. 40 has two wires sealed into its upper end, by which a spark can be passed through the gaseous mixture. The tube having been first filled with mercury, a quantity of hydrogen sufficient to occupy about one-third of the closed limb is introduced, and is followed by a volume of oxygen exactly half as great. It is more convenient to prepare a mixture of the gases in the right proportions in a separate jar, fitted with a tap at the top, from which it can be transferred to the eudiometer; and, still better, to obtain the mixture by the electrolysis of water. The gases having been introduced, and the tube erected upon a firm stand, a wider glass tube, provided with corks at the top and bottom, is passed over the eudiometer, and by means of suitable tubes a current of steam from a small boiler is passed through this outer envelope, so as to heat the tube containing the gases to the temperature of boiling water. As the gas expands mercury may be drawn off from the tap at the side, so that the metal may ultimately stand at the same level on both sides. When equilibrium has been established, and the gas expands no further, the open end of the tube is closed firmly by a cork, and a spark passed between the wires. No sound is heard, but a flash is seen, and on removing the cork and pouring

Fig. 39.

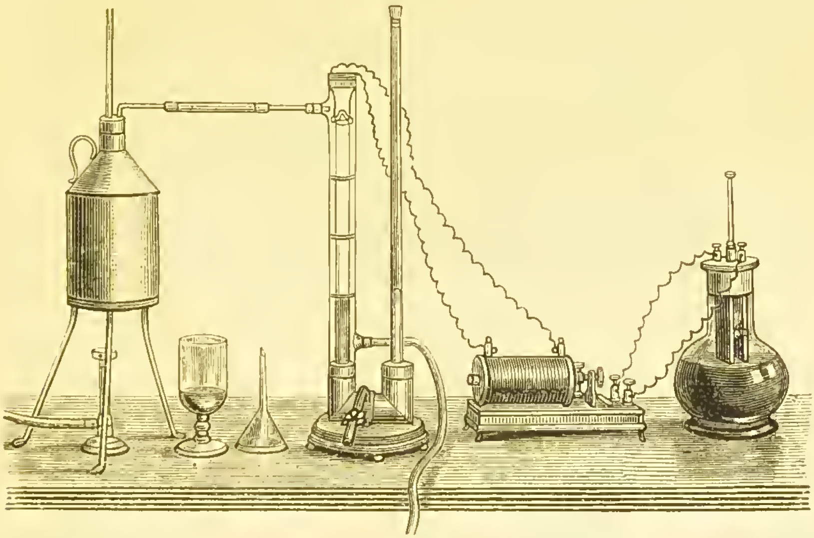


in mercury to restore the level, it will be seen that the steam produced occupies just two-thirds of the space filled by the mixture of oxygen and hydrogen from which it was formed. It may therefore be stated that steam contains a quantity of hydrogen equal in volume to itself, and half its volume of oxygen.

Properties of Water.—Pure water is colourless and transparent, destitute of taste and odour, and an exceedingly bad conductor of electricity. It attains its greatest density towards 4·5° C. (40° F.), freezes at 0° C. (32° F.), and boils under the ordinary atmospheric pressure at or near 100° C. (212° F.). It evaporates at all temperatures. The density of ice is 0·9175; water, therefore, on freezing, expands by $\frac{1}{11}$th of its volume.

The weight of a cubic centimetre of water at the maximum density is chosen as the unit of weight of the metrical system, and called a gram;

Fig. 40.



consequently a litre or cubic decimetre = 1000 cubic centimetres of water at the same temperature, weighs 1000 grams, or 1 kilogram.

A cubic inch of water at 62° F. weighs 252·45 grains; a cubic foot weighs nearly 1000 ounces avoirdupois; and an imperial gallon weighs 70,000 grains, or 10 lbs. avoirdupois.

Water is 825 times heavier than air. To all ordinary observation it is incompressible; but it does yield to a small extent when the power employed is very great, the diminution of volume for each atmosphere of pressure being about 51-millionths of the whole.

Clear water, though colourless in small bulk, is blue like the atmosphere when viewed in mass. This is seen in the deep ultramarine tint of the ocean, and perhaps in a still more beautiful manner in the lakes of Switzerland and other Alpine countries, and

in the rivers which issue from them, the slightest admixture of mud or suspended impurity destroying the effect. The same magnificent colour is visible in the fissures and caverns found in the ice of the glaciers, which is usually extremely pure and transparent within, although foul upon the surface.

Water never occurs in nature in a state of purity : even the rain which falls in the open country brings down with it small quantities of the gases of the atmosphere, beside small quantities of ammonium nitrate and the alkaline salts which, in fine particles, are carried by the wind from the sea to be dispersed widely over the land. Water has such extensive solvent powers that it no sooner falls upon the ground than it dissolves, more or less freely, the components of the soil, partly in virtue of their solubility in water, partly by the assistance of the carbonic acid dissolved out of the air. Hence the water of rivers, springs, and of the sea are contaminated to a greater or less extent by soluble matters partly earthy or saline, partly of organic origin.

The following tables will convey some idea of the nature of the impurities thus introduced, and the extent to which they may be present in natural waters of different kinds.

Composition of Rain Water.

Seventy-one Samples collected at Rothamstead, 1869–1872.

Parts per 100,000.	Total Solids.	Organic Carbon.	Organic Nitrogen.	Ammonia.	Nitrogen as Nitrate and Nitrite.	Chlorine as Chloride.
Minimum, .	0·62	·021	·003	·005	0	0
Maximum, .	8·58	·372	·121	·155	·044	1·65
Average, .	3·42	·095	·021	·049	·007	0·33
Collected near Hyde Park, November 8, 1873.						
	2·76	·383	·040	·210	·008	·5

One impurity constantly present in the rain water falling in towns is derived from the sulphur occurring in coal. When burnt a large part of this finds its way into the air in the form of sulphurous and sulphuric acids, from 2 to 7 or 8 parts of the latter acid in 100,000 of water having been found in the rain of different towns in the United Kingdom.

Water used for drinking is supplied from a variety of sources, from lakes and rivers, from wells deriving their water from the superficial layers of soil (shallow wells), and from wells several hundred feet in depth (deep wells) which are charged with water which has undergone more or less complete purification by filtration through a considerable thickness of porous earth. As these sources

of water supply are necessarily situated in localities in which the geological strata are very diverse in character and in chemical composition, it is difficult to present, in the space at our disposal, a sufficient statement of the composition of these waters.

The student must understand, therefore, that in the following table a selection is given of only a few cases which may be regarded

COMPOSITION OF DRINKING WATERS.

Upland Surface Waters.

Parts per 100,000.	Total Solids.	Organic Carbon.	Organic Nitrogen.	Ammon.	Nitrogen as Nitrates and Nitrites.	Chlorine as Chloride.
Thirlmere Lake, . (Manchester water).	2·66	·194	·004	·003	·002	·52
Loch Katrine, . (Glasgow water).	2·80	·149	·025	·000	·004	·72
Sheffield Water, .	8·36	·356	·057	·001	·032	·85
Chester Water, .	16·84	·219	·043	·000	·000	2·00
Gloucester Water, .	24·82	·375	·042	·000	·026	1·52
Deep Wells.	*Waters from Deep Wells and Springs.*					
Nottingham, . . (New Red Sandstone).	26·04	·027	·007	·002	·817	1·50
Northampton, . . (Lias).	57·76	·168	·024	·003	·000	5·15
Eastbourne . . (Green sand).	43·12	·058	·010	·004	·130	10·00
Brighton, . . (Chalk).	30·24	·048	·009	·000	·644	3·10
London, . . . (Kent Co. Chalk).	38·80	·069	·016	·000	·329	2·30
Braintree, . . (Chalk below London clay).	106·70	·068	·033	·094	·000	38·80
Springs.						
Plymouth, . . (Granite and Gneiss).	3·50	·050	·019	·000	·000	1·30
Cheltenham, . . (New Red Sandstone).	21·22	·123	·036	·000	·305	1·35

as representative, and that great variations of composition are observed. The suitability of water for drinking cannot always be

safely inferred from the results of its chemical analysis. All the circumstances of its origin will have to be carefully considered, and especially the possibility of contamination by sewage or other organic filth.

As to the inorganic constituents commonly to be found in natural water, it is obvious that they will vary in composition as well as in amount, as shown by the foregoing tables, according to the nature of the earthy materials through which the water has percolated. In some cases the saline matters accumulate to such an extent as to give the water a perceptible taste, and confer upon it medicinal properties. One example of this kind is afforded by the well-known Cheltenham mineral water, which has been recently analysed by Professor T. E. Thorpe (*Trans. Chem. Soc.*, 1894). The results for one of the wells may be quoted.

Pitville Well, No. 3.

Saline Constituents.	Parts per 1000.	Grains per Gallon.
Sodium chloride, . .	6·6164	466·470
Sodium bromide, . .	0·0055	0·388
Sodium iodide, . . .	0·0014	0·099
Sodium sulphate, . .	1·6326	115·095
Sodium silicate, . .	0·0420	2·961
Sodium bicarbonate, . .	0·5527	38·967
Potassium sulphate, . .	0·0641	4·520
Lithium chloride, . .	Traces	Traces
Calcium carbonate, . .	0·0650	4·583
Calcium phosphate, . .	Traces	Traces
Magnesium carbonate, .	0·1544	10·886
Manganous carbonate, .	Traces	Traces
Ferrous carbonate, . .	0·0008	0·056
Aluminium phosphate, .	Traces	Traces
Ammonium bicarbonate, .	0·0011	0·078
Organic matter, . .	Traces	Traces
	9·1360	644·103
Free CO_2 at 15·5° (60° F) and 760 mm. (30 in.) =	126·785 cc.	35·31 cub. in.

Sea water, which is made up of the drainage from the land in the form of rivers concentrated by evaporation, is necessarily rich in salts. Common salt is still obtained in some countries by evaporation of sea water.

The following results of the analysis of the water of the Irish Channel by Thorpe and Morton (1870) will give a sufficiently good idea of the composition of sea water. But even in the case of sea water, the composition will vary within somewhat wide limits in seas which, like the Baltic and Mediterranean, are more or less surrounded by land, for the proportion of salt will depend upon the amount of fresh water poured into the basin by rivers. It may be

stated that water of the open sea contains, practically, a quarter of a pound of common salt in a gallon.

Results of Analysis = parts per 1000.

Sodium chloride, ...	26·439
Potassium chloride, . . .	0·746
Magnesium chloride, ...	3·150
Magnesium bromide, ...	0·070
Magnesium sulphate, ...	2·066
Magnesium carbonate, ...	Trace
Magnesium nitrate, ...	0·002
Calcium sulphate, ...	1·331
Calcium carbonate, ...	0·047
Lithium chloride, ...	Trace
Ammonium chloride, ...	0·0004
Ferrous carbonate, ...	0·005
Silica, ...	Trace
Total, ...	33·859

Reference has been made to the gases dissolved by water exposed to contact with air, as, for example, by rain water falling through the atmosphere. Such a solution is never fully saturated, and the quantity of carbon dioxide taken up depends, to a large extent, upon the amount of alkaline or earthy carbonates with which the water comes into contact. This is indicated by the figures in the following table :—

100 Vols. of Water dissolve of the following Gases—	Rain Water.	Cumberland Mountain Water.	Loch Katrine Water.	Thames Water.	Deep Chalk Well Water.
	Vols.	Vols.	Vols.	Vols.	Vols.
Nitrogen, .	1·308	1·424	1·731	1·325	1·944
Oxygen, . .	·637	·726	·704	·588	·028
Carbon dioxide,	·128	·281	·113	4·021	5·520

Water for use in the laboratory for chemical purposes is usually purified by distillation. The process may be conducted in a copper or iron boiler (figure 41), from the head of which the steam passes into a spiral coil or worm, lined with pure tin, surrounded by cold water, forming the condenser. On a small scale, a glass retort or flask may be used, with a Liebig condenser, which consists of a straight tube passing through a wider one, supplied with cold water, as shown in figure 42.

Chemical Relations of Water.—Water acts on many oxides, both acid and basic, with great energy and considerable evolution of heat, producing compounds called h y d r o x i d e s, which contain

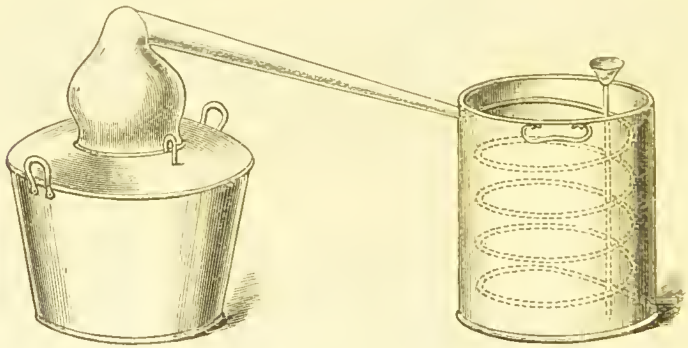
hydrogen and oxygen in the proportion to form water, but not actually existing as water, the elements of the two bodies in combining having undergone a change of arrangement thus:—

$K_2O + H_2O = 2KHO$, Potassium hydroxide (potash).
$CaO + H_2O = CaH_2O_2$, Calcium hydroxide (slaked lime).
$SO_3 + H_2O = SH_2O_4$, Sulphuric hydroxide (sulphuric acid).
$P_2O_5 + H_2O = 2PHO_3$, Phosphoric hydroxide (metaphosphoric acid).

In many of these compounds the elements of water are retained with great tenacity, and require a high temperature to expel them; calcium hydroxide, for example, requires a red heat to convert it into anhydrous calcium oxide (quicklime), and the hydroxides of potassium, barium, and phosphorus cannot be completely dehydrated by heat alone.

In other cases water appears to combine with other bodies—salts, for example—as such, or, in other words, without alteration of

Fig. 41.



atomic arrangement. Such compounds are called *hydrates*, and the water contained in them—the presence of which has great influence on the crystalline form of the compound—is called *water of crystallisation*. Water thus combined is easily expelled by heat, mostly at 100° to 120°. The dry substance deprived of water is said to be *anhydrous*.

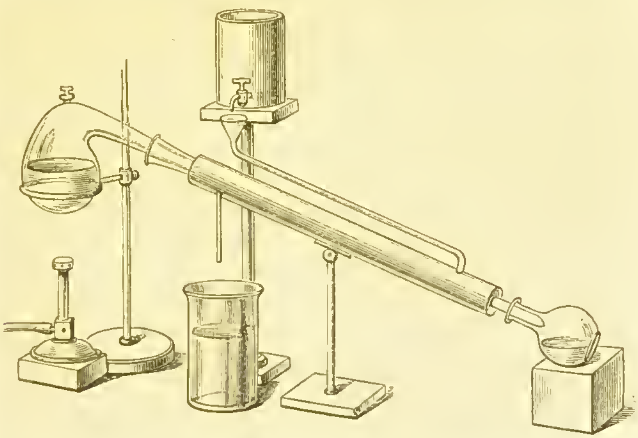
Many salts combine with different quantities of water, according to the temperature at which they separate from solution, the quantity thus taken up being for the most part greater as the temperature of solidification is lower: thus sodium carbonate crystallises from solution at ordinary temperatures in oblique rhombic prisms containing 10 molecules of water ($Na_2CO_3 + 10H_2O$), whereas at higher temperatures it crystallises as $Na_2CO_3 + 7H_2O$, and from a boiling solution in rectangular plates containing $Na_2CO_3 + H_2O$.

In many cases remarkable changes of colour are observed in passing from one hydrate to another, as in the addition of water

to an anhydrous compound. Thus the compound $CuSO_45H_2O$ constitutes blue vitriol; anhydrous copper sulphate $CuSO_4$ is white. Cupric chloride crystallised with water, $CuCl_22H_2O$, has a pale blue colour; the anhydrous chloride, $CuCl_2$, is yellowish-brown. Cobalt iodide can appear in three forms—anhydrous, CoI_2, as a black solid, with two proportions of water $CoI_2.2H_2O$ as green crystals, and with six proportions CoI_26H_2O as red crystals.

In some cases water of crystallisation is so feebly combined that it gradually separates when the substance containing it is exposed at ordinary temperatures to dry air, the salt at the same time losing its crystalline character and falling to powder. This change, called efflorescence, is strikingly exhibited by crystallised sodium carbonate and sodium phosphate. On the other hand, many substances which are very soluble in water attract water from moist air in such

Fig. 42.



quantity as to form a solution; this change, which is exhibited by calcium chloride and potassium hydroxide (caustic potash), is called deliquescence.

Solution of Solids.

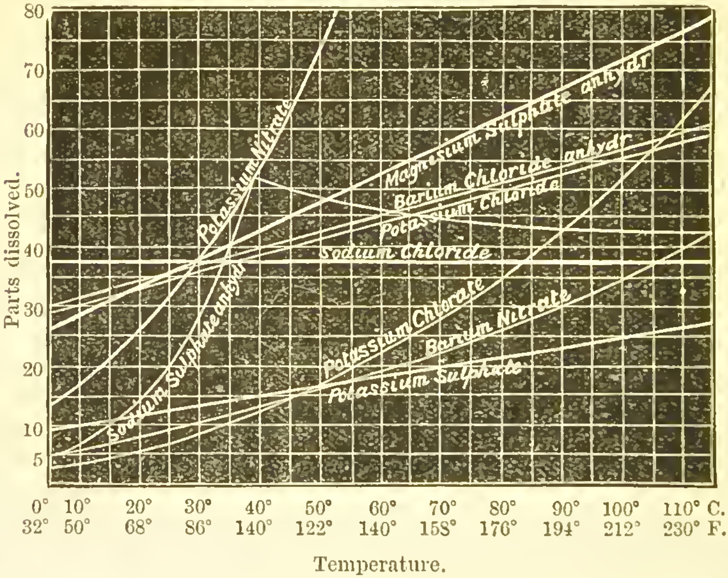
The solvent properties of water far exceed those of any other liquid known. Among salts a very large proportion are soluble to a greater or less extent, the solubility usually increasing with the temperature, so that a hot saturated solution deposits crystals on cooling. There are a few apparent exceptions to this law, one of the most remarkable of which is common salt, the solubility of which is nearly the same at all temperatures; the hydroxide and certain organic salts of calcium also dissolve more freely in cold than in hot water.

The solubility of a salt is usually represented by the quantity of anhydrous salt dissolved by 100 parts of water. Figure 43

exhibits a graphic method of displaying and comparing the solubility of different salts in water of different temperatures. The *lines of solubility* cut the verticals raised from points indicating the temperatures upon the lower horizontal line, at heights proportioned to the quantities of salt dissolved by 100 parts of water. The diagram shows, for example, that 100 parts of water dissolve, of potassium sulphate 8 parts at 0° C., 17 parts at 50°, and 25 parts at 100°. Sodium chloride possesses nearly the same degree of solubility in water at all temperatures; in other cases, potassium sulphate or potassium chloride, for example, the solubility increases almost directly with the increment of temperature; in others, again, like potassium nitrate or potassium chlorate, the solubility augments

Solubility of Salts in 100 *parts of Water.*

Fig. 43.



much more rapidly than the temperature. The differences in the deportment of these and other salts are shown very conspicuously by the lines and curves in the diagram.

Experiment.—Take about an ounce of nitre with an equal weight of common salt and dissolve them in about 8 ounces of warm water, contained in an evaporating basin. Support the dish upon a stand over a Bunsen flame turned low, and let the liquid evaporate till reduced to about one-fourth of its bulk. Then let it rest a moment till all crystals which have been deposited may subside to the bottom, and quickly pour off the whole of the still warm solution into another dish. The small cubic crystals left behind consist entirely of common salt. The liquid on cooling shoots into long prisms of a totally different form, consisting of nitrate of potassium.

The question what becomes of the constituents of the salt when dissolved in water is a very difficult one and cannot be fully discussed at this point. But, from the signs of chemical combination, such as evolution of heat, observed when many anhydrous salts are thrown into water, and from the fact that hydrated crystallised salts usually form solutions of the same colour as the crystals, it seems probable that in many cases, if not in all, such compounds retain their water, at least in part, when they pass into solution. The solubility of a hydrated salt also differs in some cases from that of the same salt in the anhydrous state. Again, many salts, as already observed, form more than one hydrate; and these several hydrates may also differ in their solubility. Sodium sulphate forms a hydrate $Na_2SO_4+7H_2O$, consisting, in 100 parts, of 53 parts of anhydrous salt and 47 parts of water, which is obtained in crystals when a solution of sodium sulphate, saturated at 100° C., is cooled out of contact with the air: this hydrate is much more soluble than the ordinary hydrate, $Na_2SO_4+10H_2O$ (Glauber's salt), which differs from the former in its crystalline form, and consists, in 100 parts, of 44·2 parts of anhydrous salt and 55·8 parts of water. When a solution of sodium sulphate is saturated at the boiling point of water, and cooled to the common temperature without depositing any crystals, the salt is supposed to exist in the form of the more soluble hydrate. This salt, coming in contact with the dust of the air, or with a small crystal of common Glauber's salt, is suddenly transformed into the less soluble hydrate, part of which separates from the solution in the form of Glauber's salt. From 0° to 33° C. sodium sulphate dissolves as Glauber's salt, the solubility of which increases with the temperature; hence the rapid rise of the curve representing the solubility of the salt. Above 33° C. the hydrate of sodium sulphate is decomposed, even in solution, being more and more thoroughly converted into the anhydrous salt as the temperature increases. Sodium sulphate appears, however, far less soluble in the anhydrous state, and hence the diminution of solubility of the salt when its solution is heated above 33° C.

When water is heated in a strong vessel to a temperature above that of the ordinary boiling point, its solvent powers are still further increased. Tilden and Shenstone have traced the solubility of a number of salts in water at temperatures above the usual boiling point, and have shown that in the case of some of the more fusible salts, such as silver nitrate, the solubility becomes practically infinite at temperatures approaching the melting points of the salts. The solubility of many salts, especially these of the heavy metals, cannot be determined at these higher temperatures, because chemical decomposition takes place and new compounds are formed by the interaction of the water and the salt.

Turner enclosed in the upper part of a high-pressure steam-boiler, worked at 149° C. (300° F.), pieces of plate and crown glass. At the expiration of four months the glass was found completely corroded by the action of the water; what remained was a white mass of silica,

destitute of alkali, while stalactites of siliceous matter, above an inch in length, depended from the little wire cage which enclosed the glass. This experiment tends to illustrate the changes which may be produced by the action of water at a high temperature in the interior of the earth upon felspathic and other rocks. The phenomenon is manifest in the Geyser springs of Iceland, which deposit siliceous sinter.

Experiment.—1. Mix some Glauber's salt in a test-tube with about one-tenth of its weight of water. Place the bulb of a thermometer in the mixture, and warm the tube gently till the temperature of 33° to 34° is reached. The crystals dissolve. Now remove the thermometer and heat the liquid till it boils. A copious deposit of small crystals of sodium sulphate, Na_2SO_4, will be produced.

2. Dissolve a quantity (2 or 3 ounces) of sodium sulphate, or better, of alum, by the aid of gentle heat in about half its weight of water, contained in a small flask. Filter the liquid whilst hot into a second flask, and allow it to cool. If sufficient care has been taken to remove or dissolve every particle of the solid, the solution will not deposit crystals. But, on dropping in a small particle of the crystallised salt, and frequently, by mere exposure to the dust of the air, which probably contains particles of the same compound, crystallisation at once ensues, and the whole speedily solidifies. A liquid in this condition is said to be "supersaturated."

Absorption of Gases.

Water likewise dissolves gases. Solution of gases in water (or in other liquids) is called *absorption*, unless this solution gives rise to the formation of chemical compounds in definite proportions. The phenomena of absorption were studied by Bunsen, to whom we are indebted for the first accurate examination of this subject.

Water dissolves very unequal quantities of the different gases, and very unequal quantities of the same gas at different temperatures. 1 vol. of water absorbs, at the temperatures stated in the table, and under the pressure of 1 atmosphere, the following volumes of different gases, measured at 0° C. and 760 mm. pressure. The values for 0° are usually referred to as the coefficients of absorption of the several gases:—

	Oxygen.	Nitrogen.	Hydrogen.	Nitrogen Monoxide.	Carbon Dioxide.
0° C. . .	0·041	0·020	0·019	1·31	1·80
10° . .	0·033	0·016	0·019	0·92	1·18
20° . .	0·028	0·014	0·019	0·67	0·90

	Chlorine.	Hydrogen Sulphide.	Sulphurous Oxide.	Hydrogen Chloride.	Ammonia.
0° C. . .	—	4·37	53·9	505	1180
10° . .	2·59	3·59	36·4	472	898
20° . .	2·16	2·91	27·3	441	680
30° . .	1·75	2·33	20·4	412	536
40° . .	1·37	1·86	15·6	387	444

When the pressure increases, a larger quantity of the gas is absorbed. Gases moderately soluble in water follow in their solubility the law of Henry and Dalton, according to which the quantity of gas dissolved is proportional to the pressure. At 10° C. 1 vol. of water absorbs, under a pressure of 1 atmosphere, 1·18 vol. of carbon dioxide, measured at 0° and under a pressure of 760 mm. of mercury. The quantity of carbon dioxide dissolved under a pressure of 2 atmospheres, and measured under conditions precisely similar to those of the previous experiments, equals 2·36 vols. Again, 1 vol. of water dissolves, under a pressure of $\frac{1}{2}$ atmosphere, 0·59 vol. of carbon dioxide also measured at 0° and under 760 mm. of mercury. Gases which are exceedingly soluble in water do not obey this law, except at high temperatures, when the solubility has been already considerably diminished.

It deserves, however, to be noticed, that the pressure which determines the rate of absorption of a gas is by no means the general pressure to which the absorbing liquid is exposed, but that pressure which the gas under consideration would exert if it were alone present in the space with which the absorbing liquid is in contact. Thus, supposing water to be in contact with a mixture of 1 vol. of carbon dioxide and 3 vols. of nitrogen, under a pressure of 4 atmospheres, the amount of carbon dioxide dissolved by the water will not be equal to that which the water would have absorbed if it had been, at the same pressure of 4 atmospheres, in contact with pure carbon dioxide. In a mixture of carbon dioxide and nitrogen in the stated proportions, the carbon dioxide exercises only $\frac{1}{4}$, the nitrogen only $\frac{3}{4}$, of the total pressure of the gaseous mixture (4 atmospheres); the partial pressure due to the carbon dioxide is in this case 1 atmosphere, that due to the nitrogen 3 atmospheres; and water, though exposed to a pressure of 4 atmospheres, cannot, under these circumstances, absorb more carbon dioxide than it would if it were in contact with pure carbon dioxide under a pressure of 1 atmosphere.

It is necessary to bear this in mind in order to understand why the air which is absorbed by water out of the atmosphere differs in composition from atmospheric air. The latter consists very nearly of 21 vols. of oxygen and 79 vols. of nitrogen. In atmospheric air which acts under a pressure of 1 atmosphere, the oxygen exerts a partial pressure of $\frac{21}{100}$, the nitrogen a partial pressure of $\frac{79}{100}$ atmosphere. At 10° C. 1 vol. of water (see the above table) absorbs 0·033 vol. of oxygen and 0·016 vol. of nitrogen, supposing these gases to act in the pure state under a pressure of 1 atmosphere. But under the partial pressures just indicated, water of 10° C. cannot absorb more than $\frac{21}{100} \times 0{\cdot}033 = 0{\cdot}007$ of oxygen, and $\frac{79}{100} \times 0{\cdot}016 = 0{\cdot}013$ vol. of nitrogen. In $0{\cdot}007 + 0{\cdot}013 = 0{\cdot}020$ vol. of the gaseous mixture, absorbed by water there are consequently 0·007 vol. of oxygen, and 0·013 vol. of nitrogen, or in 20 vols. of this mixture, 7 vols. of oxygen and 13 vols. of nitrogen, or in 100 vols. of the gaseous mixture, 35 vols. of oxygen, and 65 vols. of nitrogen. The air contained at

the common temperature in water is thus seen to be very much richer in oxygen than ordinary atmospheric air.

It has even been proposed to apply this property of water to absorb oxygen from the air more readily than nitrogen to the preparation of oxygen for industrial use. Air pressed into water by means of a forcing-pump, and the gases which escape on diminishing the pressure subjected to the same treatment eight times in succession yields a mixture which consists chiefly of oxygen. The following table shows the composition of the gaseous mixture at each successive stage :—

Atmospheric Air.	Composition after successive Pressures.							
	1	2	3	4	5	6	7	8
N . . 79	66·67	52·5	37·5	25·0	15·0	9·0	5·0	2·7
O . . 21	33·33	47·5	62·5	75·0	85·0	91·0	95·0	97·3

Water containing a gas in solution, when exposed in a vacuum or in a space filled with another gas, allows the gas absorbed to escape until the quantity retained corresponds with the share of the pressure belonging to the gas evolved. If the latter be constantly removed by a powerful absorbent or by a good air-pump, it is in most cases easy to separate every trace of gas from the water. The same result is obtained when water containing a gas in solution is exposed in a relatively very large space filled with another gas. Water in which nitrogen monoxide is dissolved loses the latter entirely by mere exposure to the atmosphere, and the gas evolved cannot, at any moment, exert more than an infinitely small share of the pressure. If water be freed from gases by ebullition, the separation depends partly upon the diminution of the solubility by the increase of temperature, partly also upon the formation above the surface of the liquid of a constantly renewed atmosphere into which the gas still retained by the liquid may escape.

Some gases which are absorbed in large quantities and very quickly by water—hydrogen chloride, for instance—cannot be perfectly expelled either by the protracted action of another gas (exposure to the atmosphere) or by ebullition ; in such cases the liquid, still charged with gas, evaporates as a whole when it has assumed a certain composition. This composition varies, however, with the temperature if the liquid be submitted to a current of air, and with the pressure if it be boiled.

Liquids also lose the gas they contain in solution by freezing : hence the air bubbles in ice, which consist of the air which had been absorbed from the atmosphere by the water. Gas is retained by liquids at the freezing temperature only when it forms a chemical combination in definite proportion with the liquid. Water containing chlorine or sulphurous acid in solution freezes, without evolu-

tion of gas, with formation of a solid hydrate of chlorine or of sulphurous acid.

Pure water generally dissolves gases more copiously than water containing solid bodies in solution (salt water, for instance). If in some few cases exceptions are observed to take place, they appear to depend upon the formation of feeble but true chemical compounds in definite proportion; the fact that carbon dioxide is more copiously absorbed by water containing sodium phosphate in solution than by pure water, may be explained in this manner. The absorption of carbon dioxide by chalky waters has already been referred to (p. 77).

Properties of Solutions.

Liquid Diffusion. Dialysis.—When a solution having a density greater than that of water is introduced into a cylindrical glass vessel containing water, in such a manner that the two layers of liquid remain unmixed, the substance dissolved in the lower liquid will gradually pass into the supernatant water, though the vessel may have been left undisturbed, and the temperature remain unchanged. This gradual passage of a dissolved substance from its original solution into pure water, taking place notwithstanding the higher density of the substance, is called *diffusion*. The phenomena of diffusion were elaborately investigated by Graham, who arrived at very important results. Different substances, when in solutions of the same concentration, and under other similar circumstances, diffuse with very unequal velocity. Hydrogen chloride, for instance, diffuses with greater rapidity than potassium chloride, potassium chloride more rapidly than sodium chloride, and the latter, again, more quickly than magnesium sulphate; gelatin, albumin, and caramel diffuse very slowly. Diffusion is generally found to take place more rapidly at high than at low temperatures. It is more particularly rapid with crystallised substances, though not exclusively, for hydrogen chloride and alcohol are among the highly diffusive bodies; slow with non-crystalline bodies, which, like gelatin, are capable of forming a jelly, though even here exceptions are met with. Graham calls the substances of great diffusibility *crystalloïds*, the substances of low diffusibility *colloïds*. The unequal power of diffusion with which different substances are endowed frequently furnishes the means of separating them. When water is poured with caution, so as to prevent mixing, upon a solution containing equal quantities of potassium chloride and sodium chloride, the more diffusible potassium chloride travels more rapidly upwards than the less diffusible sodium chloride, and very considerable portions of potassium chloride will have reached the upper layers of the water before the sodium chloride has arrived there in appreciable quantity. The separation of rapidly diffusible crystalloïds and slowly diffusible colloïds succeeds still better.

A more complete separation of crystalloïds and colloïds may be

accomplished in the following manner:—Graham made the important observation that certain membranes, and parchment paper, when in contact, on the one surface, with a solution containing a mixture of crystalloïdal and colloïdal substances, and, on the other surface, with pure water, will permit the passage to the water of the crystalloïds, but not of the colloïds. To carry out this important mode of separation, which is designated by the term *dialysis*, the lower mouth of a glass vessel, open on both sides (fig. 44), is tied over with parchment paper, placed upon an appropriate support (fig. 45), and transferred, together with the latter, into a larger vessel filled with water (fig. 46); or the vessel may be suspended, as shown in figure 47. The liquid containing the different substances in solution is then poured into the inner vessel, so as to form a layer of about half an inch in height upon the parchment

Fig. 44.

Fig. 45

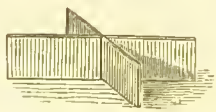


Fig. 46.

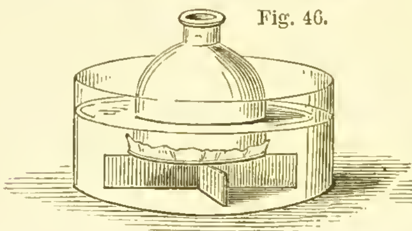
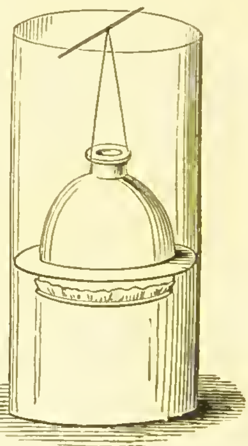


Fig. 47.



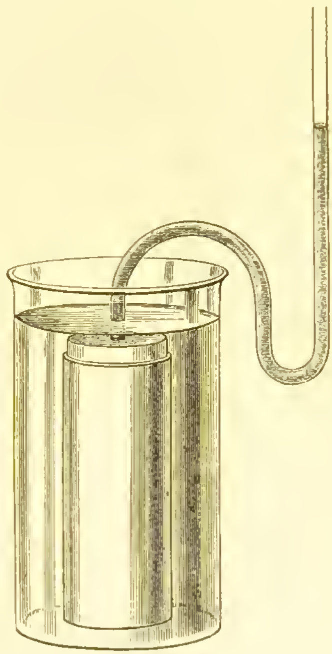
paper. The crystalloïdal substances gradually pass through the parchment paper into the outer water, which may be renewed from time to time; the colloïdal substances are almost entirely retained by the liquid in the inner vessel. In this manner Graham prepared several colloïds free from crystalloïds; he showed, moreover, that poisonous crystalloïds, such as arsenious acid or strychnine, even when mixed with very large proportions of colloïdal substances, pass over into the water of the dialyser in such a state of purity that their presence may be established by reagents with the utmost facility.

Osmose.—When two different liquids are separated by a porous diaphragm, as, for instance, by a membrane, and the liquids mix through this diaphragm, it is found that in most cases the quantities travelling in opposite directions are unequal.

Osmotic pressure.—These phenomena have been studied most satisfactorily by means of porous earthenware vessels, the pores of which

have been stopped by the deposition of a fine precipitate. Ferrocyanide of copper has usually been employed, and its deposition is easily effected by saturating a clay battery cell with copper sulphate, rinsing it out with water, and then immersing in a solution of potassium ferrocyanide. A vessel thus prepared if filled with a solution of sugar for example, allows water to pass through but not the dissolved sugar. Hence if the pot, filled with such a solution, be closed by a rubber cork through which passes a tube bent as in the figure and then immersed in water, it will be found that the liquid in the tube gradually rises till it attains a considerable height, indicating the existence of an excess of pressure within the vessel. This pressure is called Osmotic Pressure, and if the temperature is kept constant its amount is proportional to the strength of the solution. It is supposed that as the water passes freely through the membrane, while the dissolved substance passes only very slowly by diffusion, the water passes from without into the pot till the water pressure on both sides of the membrane is the same. Inside there is also the pressure exerted by the dissolved substance, which, according to the current hypothesis, behaves when in a state of solution as though its molecules moved like gaseous molecules (*see* Kinetic Theory of Gases) within the space occupied by the liquid.

Fig. 48.



Density of Solids and Liquids.

By the *density of a body* is meant the *quantity of matter* compared with the quantity of matter in an *equal volume* of some standard body arbitrarily chosen. *Specific gravity* is a term often used to denote the *weight* of a body—or the force with which it tends to fall to the earth—as compared with the weight of an equal bulk, or volume, of the standard body, which is reckoned as unity. In other words, density means comparative *mass*, and specific gravity comparative *weight*. These expressions are often used indifferently, since mass and weight are directly proportional to each other. The term *relative density* is, however, preferable to specific gravity, inasmuch as weight is a variable property depending upon the position of the body on the earth. In all cases of solids and liquids the standard

of unity adopted is pure water at the temperature of maximum density or 4° C. Anything else might have been chosen; there is nothing in water to render its adoption for the purpose mentioned indispensable: it is simply taken for the sake of convenience, being always at hand, and easily obtained in a state of purity. An ordinary expression of specific weight, therefore, is a number expressing how many times the weight of an equal bulk of water is contained in the weight of the substance spoken of. If, for example, we say that concentrated oil of vitriol has a relative density equal to 1·85, or that pure alcohol has a density of 0·794 at 15·5° C., we mean that equal bulks of these two liquids and of distilled water possess weights in the proportion of the numbers 1·85, 0·794, and 1; or 1850, 794, and 1000. It is necessary to be particular about the temperature, for, since bodies change in volume with change of temperature, a constant bulk of the same liquid will not retain a constant weight. It will be proper to begin with the description of the mode in which the density of liquids is determined: this is the simplest case, and the one which best illustrates the general principle.

Fig. 49.

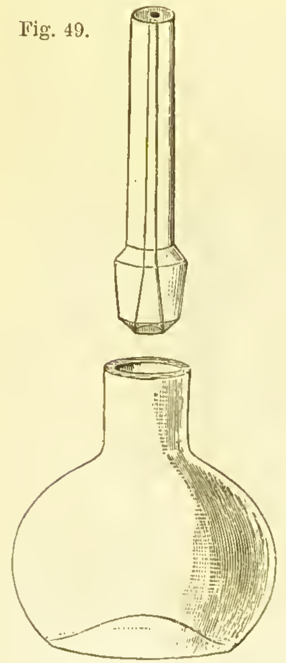
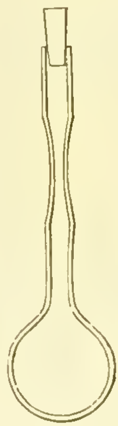


Fig. 50.



In all operations of this kind, and in the conduct of quantitative chemical analysis, the determination of weight must be made with considerable approach to accuracy. The balance usually employed is constructed of brass and all the working parts are made as light as possible, consistently with inflexibility. A balance of modern construction is shown in figure 1, p. 10.

To find the relative density of any particular liquid compared with that of water, it is only requisite to weigh equal bulks at the standard temperature, and then divide the weight of the liquid by the weight of the water; the quotient will be greater or less than unity, as the liquid experimented on is heavier or lighter than water. Now, to weigh equal bulks of two liquids, the simplest and best method is clearly to weigh them in succession in the same vessel, taking care that it is equally full on both occasions.

The vessel commonly used for this purpose is a small glass bottle provided with a perforated conical glass stopper, very accurately fitted by grinding (fig. 49). By completely filling the bottle with liquid,

and carefully removing the portion of liquid which is displaced when the stopper is inserted, an unalterable measure is obtained. The least possible quantity of grease applied to the stopper greatly promotes the exact fitting.

When the chemist has only a very small quantity of a liquid at his disposal, and wishes not to lose it, the little glass vessel (fig. 50) is particularly useful. It is formed by blowing a bulb on a glass tube. On that portion of the tube which is narrowed by drawing the tube out over a lamp, a fine scratch is made with a diamond. The bulb is filled up to this mark with the liquid while it stands in water, the temperature of which is exactly known. A very fine funnel is used for filling the bulb, the stem of the funnel being drawn out so as to enter the tube, and the upper opening of the funnel being small enough to be closed by the finger. The glass stopper is wanted only as a guard, and does not require to fit perfectly.

Another more convenient form of apparatus used in determining the density of liquids was devised by Dr Sprengel. It consists of an elongated U-tube (fig. 51), the ends of which terminate in the two capillary tubes, *a*, *b*, bent at right angles in opposite directions. The shorter one, *a*, is a good deal narrower (at least towards the end) than the longer one, the inner diameter of which is about half a millimetre. The horizontal part of this wider tube is marked near the bend with a fine line, *b*.

Fig. 51.

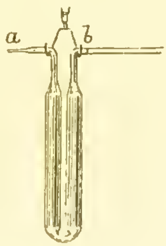
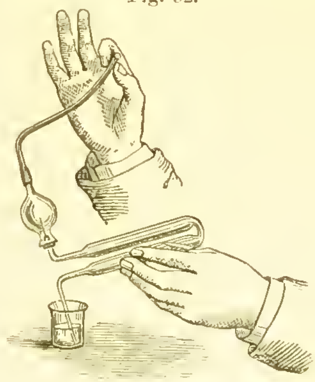


Fig. 52.



The U-tube is filled by suction—the little bulb-apparatus (fig. 52) having been previously attached to the narrow capillary tube by a piece of india-rubber tubing—then detached from the bulb, placed in water almost up to the bends of the capillary tubes, left there till it has assumed the temperature of the water, and, after careful adjustment of the volume of the liquid up to the mark *b* in the wider capillary tube, it is taken out, dried, and weighed.

The determination of the density of a solid body is also made according to the principles above explained, and may be performed with the specific-gravity bottle (fig. 49). The bottle is first weighed full of water; the solid is then placed in the same pan of the balance, and its weight is determined; finally, the solid is put into the bottle, displacing an equal bulk of water, the weight of which is determined by the loss on again weighing. Thus, the weights of the solid and

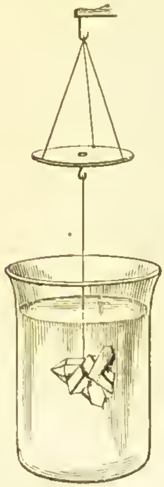
that of an equal bulk of water are obtained. The former divided by the latter gives the relative density.

For example, the weight of a small piece of silver wire was found to be, ...	6·36	grams.
Glass bottle filled with water, ...	19·09	,,
	25·45	,,
After an equal volume of water was displaced by the silver, the weight was, ...	24·85	,,
Hence the displaced water weighed, ...	0·60	,,

From this the relative density of the silver wire is, ... $\frac{6·36}{0·60} = 10·6$

Another less exact method of determining the relative density of solids, is based on the well-known theorem of Archimedes, which may be thus expressed:

Fig. 53.



When a solid is immersed in a fluid, it loses a portion of its weight; and this portion is equal to the weight of the fluid which it displaces, that is, to the weight of its own bulk of that fluid.

This principle is applied as follows:—

Let it be required, for example, to know the density of a body of extremely irregular form, as a small group of rock-crystals: the first part of the operation consists in determining its absolute weight, or, more correctly speaking, its weight in air; it is next suspended from the balance-pan by a fine horsehair, immersed completely in pure water at 15·5°, and again weighed. It now weighs less, the difference being the weight of the water it displaces, that is, the weight of an equal bulk. This being known, nothing more is required than to find, by division, how many times the latter number is contained in the former; the quotient will be the density, water at the temperature of 15·5° being taken = 1. For example:—

The quartz-crystals weigh in air, ...	19·03	grams.
When immersed in water, they weigh, . . .	11·67	,,
Difference, being the volume of an equal volume of water, ...	7·36	,,

$$\frac{19·03}{7·36} = 2·58, \text{ the density required.}$$

The rule is generally thus written: "Divide the weight in air by the loss of weight in water, and the quotient will be the relative

density." In reality it is not the weight in air which is required, but the weight the body would have in empty space : the error introduced, namely, the weight of an equal bulk of air, is so trifling that it is usually neglected.

Sometimes the body to be examined is lighter than water, and floats. In this case, it is first weighed, and afterwards attached to a piece of metal heavy enough to sink it, and suspended from the balance. The whole is then exactly weighed, immersed in water, and again weighed. The difference between the two weighings gives the weight of a quantity of water, equal in bulk to both together. The light substance is then detached, and the same operation of weighing in air, and again in water, repeated on the piece of metal. These data give the means of finding the specific gravity, as will be seen by the following example :—

Light substance (a piece of wax) weighs in air, .	8·66	grams.
Attached to a piece of brass, the whole now weighs, ...	11·90	,,
Immersed in water, the system weighs, . .	2·51	,,
Weight of water equal in bulk to brass and wax,	9·39	,,
Weight of brass in air, ...	3·24	,,
Weight of brass in water, ...	2·87	,,
Weight of equal bulk of water, ...	0·37	,,
Weight of bulk of water equal to wax and brass,	9·39	,,
Weight of bulk of water equal to brass alone, .	0·37	,,
Weight of bulk of water equal to wax alone, .	9·02	,,

$$\frac{8{\cdot}66}{9{\cdot}02} = 0{\cdot}96, \text{ the density required.}$$

In all such experiments, it is necessary to pay attention to the temperature and purity of the water, and to remove with great care all adhering air-bubbles, otherwise a false result will be obtained.

Fig. 54.

Other cases require attention in which these operations must be modified to meet particular difficulties. One of these happens when the substance is dissolved or acted upon by water. This difficulty is easily overcome by substituting some other liquid of known density which experience shows is without action. Alcohol or oil of turpentine may generally be used when water is inadmissible. Suppose, for instance, the density of crystallised sugar is required, we proceed in the following way :—The density of the oil of turpentine is first determined; let it be 0·87; the sugar

is next weighed in the air, then suspended by a horsehair, and weighed in the oil; the difference is the weight of an equal bulk of the latter; a simple calculation gives the weight of a corresponding volume of water :—

Weight of sugar in air, ...	25·92 grams.
Weight of sugar in oil of turpentine, ...	11·82 „
Weight of equal bulk of oil of turpentine, .	14·10 „

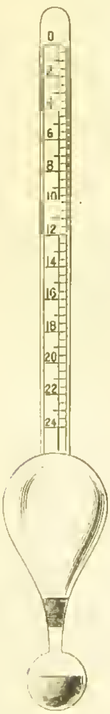
$$87 : 100 = 14{\cdot}10 : 16{\cdot}20,$$

the weight of an equal bulk of water: hence the density of the sugar,—

$$\frac{25{\cdot}92}{14{\cdot}10} = 1{\cdot}8\,.$$

If the substance to be examined consists of small pieces, or of powder, the method first described, namely, that of the specific-gravity bottle, can alone be used.

Fig. 55.



Hydrometers.—The theorem of Archimedes affords the key to the general doctrine of the equilibrium of floating bodies, of which an application is made in the common hydrometer,—an instrument for finding the relative densities of liquids in a very easy and expeditious manner.

When a solid body is placed upon the surface of a liquid specifically heavier than itself, it sinks down until it displaces a quantity of liquid equal to its own weight, at which point it floats. Thus, in the case of a substance floating in water, whose density is one-half that of the liquid, the position of equilibrium will involve the immersion of exactly one-half of the body, inasmuch as its whole weight is counterpoised by a quantity of water equal to half its volume. If the same body were put into a liquid of one-half the density of water, if such could be found, it would then sink beneath the surface, and remain indifferently in any part. A floating body of known density may thus be used as an indicator of the density of a liquid. In this manner little glass beads (fig. 54) of known densities are sometimes employed in the arts to ascertain in a rude manner the density of liquids; the one that floats indifferently beneath the surface, without either sinking or rising, has of course the same density as the liquid itself; this is pointed out by the number marked upon the bead.

The hydrometer (fig. 55) in general use consists of a floating vessel of thin metal or glass, having a weight beneath to maintain it in an upright position, and a stem above bearing a divided scale. The liquid to be tried is put into a small narrow jar, and the

instrument floated in it. It is obvious that the denser the liquid, the higher will the hydrometer float, because a smaller displacement of liquid will counterbalance its weight. For the same reason, in a liquid of less density, it sinks deeper. The hydrometer comes to rest almost immediately, and then the mark on the stem at the fluid-level may be read off.

Very extensive use is made of instruments of this kind in the arts: they sometimes bear different names, according to the kind of liquid for which they are intended; but the principle is the same in all. The graduation is very commonly arbitrary, two or three different scales being unfortunately used. These may be sometimes reduced, however, to the true numbers expressing the relative density by the aid of tables of comparison drawn up for the purpose.

THE HALOGEN GROUP OF ELEMENTS.

THIS group includes chlorine, bromine, and iodine. Fluorine is closely related to these elements, but exhibits many anomalous characters. They are all gaseous or vaporisable substances, which unite readily with metals and with hydrogen, but do not combine directly with oxygen, and their known compounds with that element are more or less unstable. Their compounds with hydrogen are very characteristic of the group, being all colourless fuming gases, very soluble in water, having an acid taste and acting strongly on metals and metallic oxides. These gases all consist of equal volumes of the gaseous element and hydrogen united without contraction.

These elements, ranged in the order of their chemical relations, exhibit a remarkable connection between their atomic weights, bromine, the intermediate element, standing almost exactly midway between chlorine and iodine. Thus :—

	Atomic Weight.
Chlorine,	35·4
Bromine,	80
Iodine,	127

The arithmetical mean of the atomic weights of chlorine and iodine is

$$\frac{35{\cdot}4 + 127}{2} = 81{\cdot}2 .$$

On account of the occurrence of chlorine, bromine and iodine in the salts contained in sea-water, the elements of this group are called halogen-elements, and their metallic compounds, haloïd compounds.*

CHLORINE.

Symbol, Cl. Atomic weight, 35·4. Density, 35·4.

Chlorine is a greenish yellow gas discovered by Scheele in 1774. It was supposed by Lavoisier to contain oxygen, but was shown by H. Davy to be a simple substance incapable of chemical decomposition, and from him it received the name chlorine, in allusion to its colour (χλωρός).

Experiment.—Chlorine is most easily prepared by pouring strong hydrochloric acid upon finely powdered black oxide of manganese (MnO_2) contained in a retort or flask (fig. 56), and applying a gentle

* From ἅλς, f., the sea ; ἅλς, m., salt.

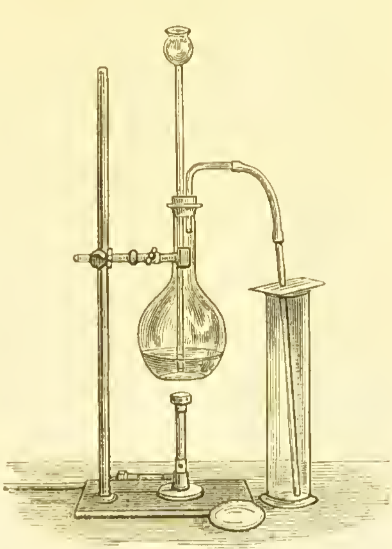
heat; the chlorine then passes over in the form of a heavy yellow gas, which may be collected over warm water, or by displacement of air: the mercurial trough cannot be employed, as chlorine rapidly acts upon the metal, and is absorbed.

The reaction consists in the formation of an unstable chloride of manganese, which is decomposed by heat. Water is also formed, while of the chlorine, one-half unites with the manganese, forming a chloride, $MnCl_2$, and the other half is given off as gas:

$$\begin{aligned} MnO_2 + 4\,HCl &= MnCl_4 + 2H_2O \\ &= MnCl_2 + Cl_2 + 2H_2O. \end{aligned}$$

The same process is used for the preparation of chlorine on the manufacturing scale, the hydrochloric acid which is evolved in large quantities by heating common salt with sulphuric acid, in Leblanc's soda-process, being utilised for the purpose.

Fig. 56.



A process for obtaining chlorine from hydrochloric acid, without the use of any manganese compound, was introduced by the late Mr H. Deacon. It consists in passing a mixture of hydrochloric acid gas and oxygen, or air, over cupric sulphate or other cupric salt heated to 370–400° C. (698–752° F.), the hydrochloric acid being then decomposed, its hydrogen combining with the oxygen, and the chlorine being set free. The best way of conducting the process is to pass the mixed gases over pieces of brick soaked in solution of cupric sulphate and dried. The action of the copper salt is not well understood, but appears to belong to that class of phenomena called catalytic or contact actions, in which the catalytic agent undergoes a succession of changes, though finally restored to its original condition. Other metallic salts act in a similar way, but less completely.

Another process which has even found a place among manufacturing operations upon a large scale, is based upon the fact that chloride of magnesium, $MgCl_2$, is decomposed when heated strongly in a current of air. Oxygen is absorbed, the magnesium converted into the oxide, MgO, and chlorine liberated in the gaseous state. The method, so far as at present adopted, is associated with the manufacture of soda by the ammonia process, and with the production of chlorates, an account of which will be given later in the book.

The process, which now seems likely to take an important posi-

tion, if not to displace all the others for manufacturing purposes, is based upon the decomposition of sodium chloride or common salt dissolved in water by current electricity. The products are chlorine and hydrogen gases, which can be separately collected, and caustic soda, NaHO, which remains in solution. The process is already worked upon a manufacturing scale, the electric current being produced by dynamo-machines, often driven by water power, and the brine operated upon can be pumped direct from a salt mine.

Chlorine is a yellow gaseous body, of intolerably suffocating properties, producing very violent cough and irritation when inhaled, even in exceedingly small quantity. It is soluble to a considerable extent in water, that liquid absorbing at 15·5° about twice its volume, and acquiring the colour and odour of the gas. When moist chlorine gas is exposed to a temperature of 0°, yellow crystals are formed, which consist of a definite compound of chlorine and water, containing 35·4 parts of the former to 90 of the latter, or $Cl_2.10H_2O$.

Chlorine has a density of 2·45 (air = 1); a litre of it weighs 3·167 grams; exposed to a pressure of about four atmospheres, it condenses to a yellow limpid liquid. It is now commonly sold in a liquid state contained in steel cylinders fitted with a screw tap, by which it may be drawn off very conveniently for laboratory use. Figure 57 shows one of these vessels.

Fig. 57.

Chlorine has but little attraction for oxygen, its energies being principally exerted towards hydrogen and the metals.

Experiments.—Collect several jars of chlorine by the process already described. 1. To show its combination with hydrogen take a small gas cylinder, fill it with water in the pneumatic trough, and displace exactly half the water by hydrogen gas. Then displace the remainder of the water by chlorine. Close the jar by a glass plate, shake it in order that the hydrogen and chlorine may be completely mixed, then remove the plate and apply a flame. A sharp explosion follows, the colour of the chlorine disappears, and hydrogen chloride gas, recognisable by its steamy fumes, is formed.

2. Attach a small taper to a wire, light it, and lower it into a bottle of chlorine. Much black smoke is formed, consisting of the carbon of the wax. The hydrogen unites with the chlorine.

3. Further to illustrate the action of chlorine upon hydrogen and its inability to combine directly with carbon, wet a strip of filter-paper or linen with turpentine oil, and plunge it quickly into pure chlorine. The chemical action of the latter is so violent as to cause flame accompanied by copious deposit of soot.

Chlorine has so strong an attraction for hydrogen, that it is even capable of decomposing water, liberating oxygen. If a bottle or jar filled with strong chlorine water, and inverted into a dish containing the same solution, be placed in a position in which it may receive the direct rays of the sun, the liquid soon loses its yellow colour and peculiar odour, and becomes capable of reddening instead of bleaching litmus paper, at the same time a small quantity of gaseous oxygen is liberated. The latter may be recognised by its want of colour and by rekindling a splinter of wood, the tip of which has been ignited, and the flame extinguished, leaving only a spark. The decomposition may be expressed by the equation—

$$Cl_2 + H_2O = 2HCl + O.$$

The same change may be effected more readily, and oxygen obtained in considerable quantities, by transmitting through a glass or porcelain tube, heated to bright redness, a mixture of chlorine and vapour of water.

Experiment.—The very characteristic bleaching action of chlorine depends upon its attraction for hydrogen. Wet a piece of blue litmus paper, or cotton print, with water, and place it in contact with chlorine. It is almost instantly bleached. The presence of water is essential, for the gas when absolutely dry is almost destitute of action.

Chlorine is largely used in the arts for bleaching linen and cotton goods, rags for the manufacture of paper, etc. For these purposes, it is employed sometimes in the state of gas, sometimes in that of aqueous solution, but more frequently in combination with lime, forming the substance called bleaching-powder. It is also one of the best and most potent substances than can be used for the purpose of disinfection, but its employment requires care. Bleaching-powder mixed with water, and exposed in shallow vessels, is slowly decomposed by the carbonic acid of the air, and chlorine, or an oxide of chlorine, is evolved: if a more rapid disengagement be wished, a little acid may be added. In the absence of bleaching-powder, the production of the gas may be effected by exposing in a dish a mixture of common salt, manganese dioxide, and sulphuric acid diluted with an equal bulk of water.

The action of chlorine upon metals is generally very vigorous, the rate of action being increased by extending the surface of the metal, as when very thin foil or fine powder is used. Many metals combine with chlorine in several proportions. The compounds formed are called chlorides.

Experiment.—Throw into a flask full of chlorine a little powdered antimony. The metal burns with a whitish flame, and on cooling the smoke will be found to collect on the sides of the glass in the form of a crystalline deposit, consisting chiefly of the chloride $SbCl_3$.

Hydrogen Chloride, or **Hydrochloric Acid**, HCl; formerly called *Muriatic Acid.*—This substance, in the state of solution in

water, has long been known. The gas is easily prepared by heating a mixture of common salt and sulphuric acid ; it must be collected by displacement, or over mercury. It is a colourless gas, which fumes strongly in the air from condensing the atmospheric moisture; it has an acid, suffocating odour, but is much less offensive than chlorine. Exposed to a pressure of 40 atmospheres, it liquefies.

Hydrogen chloride acid gas has, according to experiment, a density 1·278 compared with air, or 18·44 compared with hydrogen as unity, the calculated number being $\frac{35\cdot4 + 1}{2} = 18\cdot2$. It is exceedingly soluble in water, that liquid taking up, at the temperature of the air, about 418 times its bulk. The gas and solution are powerfully acid.

The action of sulphuric acid on common salt is explained by the equations which follow.

In the first place, supposing an excess of salt to be used, a part of it is converted into sodium hydrogen sulphate, thus

$$NaCl + H_2SO_4 = HCl + NaHSO_4.$$

Subsequently, on the application of heat, this acid sulphate decomposes an additional quantity of salt equal to the first, and neutral sulphate of sodium results,

$$NaCl + NaHSO_4 = HCl + Na_2SO_4.$$

In the manufacture of sodium sulphate, called "salt-cake," these two operations are quite distinct. On the small scale it is better to use a slight excess of sulphuric acid, so that the residue shall consist of the more fusible and soluble acid sulphate.

Experiments.—Let the flask used in making chlorine be thoroughly cleansed. Put into it about an ounce of common salt, replace the cork with the funnel and conducting tube, and arrange a dry jar as before. Now pour slowly through the funnel about a fluid ounce of sulphuric acid. The hydrogen chloride gas is at once evolved, and may be led into jars placed successively for its reception.

1. Having collected a jar full of the gas, close it by a ground-glass plate, and place the mouth beneath the surface of water in a pneumatic trough. On removing the glass plate the water will ascend rapidly, and, if the gas were quite free from air, would fill the jar completely.

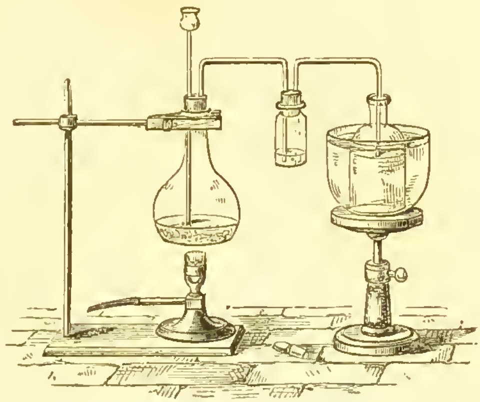
2. Apply a lighted taper to a jar full of the gas. The light is extinguished, and the gas does not take fire.

3. Hold a piece of blue litmus paper in the gas. It is immediately reddened, but it is not bleached, even when left for some time in contact with the gas.

4. Prepare a saturated solution of the gas in the following manner :—To the flask, filled as before, attach a small bottle provided, as shown in figure 58, with a conducting tube, by which the gas as it

passes from the generator is led through a small quantity of water, or better, of ordinary strong liquid hydrochloric acid. The use of this is to arrest particles of salt or of sulphuric acid that may accidentally be carried over. From this washing bottle the gas passes into some distilled water contained in a bottle, which should be immersed in cold water. If 2 ounces of common salt are taken with twice its weight of sulphuric acid, the quantity of water used for dissolving the gas should not exceed 2 ounces.

Fig. 58.



Pure solution of hydrochloric acid is transparent and colourless; when strong it fumes in the air by evolving a little gas. It leaves no residue on evaporation, and gives no precipitate or opacity with diluted solution of barium chloride. When saturated with the gas at 15°, it has a density of 1·21, and contains about 42 per cent. of real acid. The commercial acid, which is obtained in immense quantity as a secondary product in the manufacture of sodium sulphate by the action of sulphuric acid upon common salt, has usually a yellow colour, and is very impure, containing salts, sulphuric acid, chloride of iron, and arsenic. It may be rendered sufficiently pure for most purposes by diluting it to the density of 1·1, which happens when the strong acid is mixed with its own bulk or rather less of water, and then distilling it in a retort furnished with a Liebig's condenser.

On distilling an aqueous solution of hydrochloric acid, an acid is produced boiling at 110°, which contains 20·22 per cent. of anhydrous hydrogen chloride; a more concentrated solution when heated gives off hydrogen chloride; a weaker solution loses water. Roscoe and Dittmar have proved that the composition of the distillate varies with the atmospheric pressure.

A crystalline hydrate of hydrochloric acid, having the composition $HCl,2H_2O$, is formed by passing a stream of nearly dry hydrogen chloride gas through the concentrated aqueous acid cooled by a freezing mixture to $-22°$. The crystals decompose rapidly in the air, emitting white fumes.

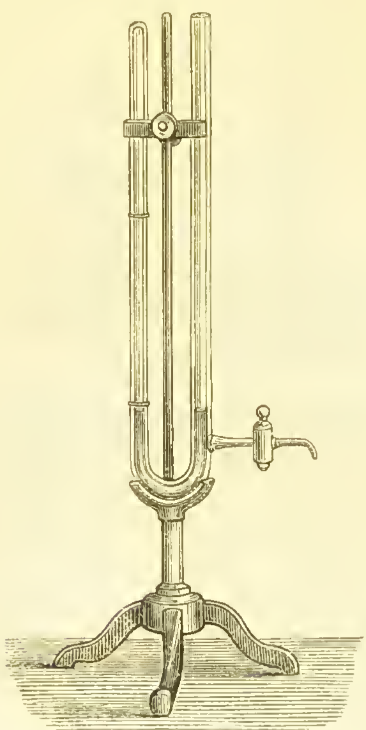
The composition of hydrogen chloride gas may be proved experimentally either by analysis or by synthesis.

In order to demonstrate the proportion of hydrogen in the gas, advantage is taken of the action of the metal sodium, which, when dissolved in mercury (forming sodium "amalgam"), is still capable

of combining with the chlorine of hydrogen chloride, liberating the hydrogen. The operation is conducted in a tube of the form represented in figure 59.

One end of the tube being closed and the other open, the closed end is first filled with dry mercury. Then the tap at the side being opened, the delivery-tube of a small flask, fitted for the generation of dry hydrogen chloride, is pushed down into the mercury, and a quantity of gas introduced into the tube so as to displace about two-thirds of the mercury from the sealed branch. The tap is then closed, and mercury poured into the open tube till it stands, as shown in the figure, at the same height on both sides, and the gas is, therefore, under atmospheric pressure. The level of the mercury being marked off by a rubber ring or strip of paper, fluid sodium amalgam, free from soda, is poured into the open tube, so as completely to fill it. The mouth of the tube being then securely closed by the thumb, the tube is inverted, so that the gas is brought freely into contact with the sodium amalgam. After being shaken for a few minutes, the whole of the gas is retransferred to the closed branch of the tube, and the thumb removed. The level of the mercury is now adjusted as before, and it will be observed that the volume of gas (hydrogen) which remains is exactly half the volume of the gas (hydrogen chloride) operated upon.

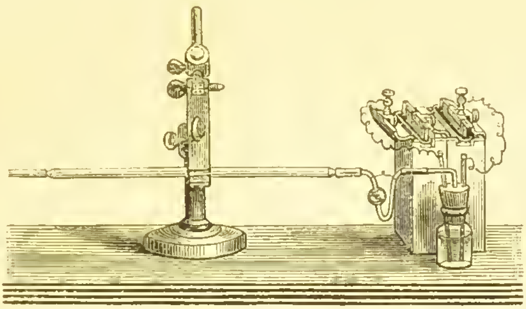
Fig. 59.



In order to demonstrate the fact that hydrogen chloride also contains half its volume of chlorine, the following method, based upon its decomposition by electrolysis, may be adopted :—The experiment must be made in a room lighted only by gas or candle. A small electrolytic cell may be constructed, as shown in the figure, by fitting to a small wide-mouthed bottle a rubber stopper, through which pass two sticks of hard carbon to serve as electrodes, and a tube to carry off the gases. The bottle is filled with ordinary strong hydrochloric acid solution, and the current from three or four Grove's cells is made to traverse the liquid. The gas evolved at first consists chiefly of hydrogen, the chlorine remaining dissolved in the liquid. But, after about ten minutes, the liquid becomes saturated with chlorine, and the two gases are evolved together. It is advisable to cause

the gas to bubble through a little water placed in a small bulb apparatus, in order to absorb hydrogen chloride which may be given off. The bottle should also be kept cool, by placing it in a dish of cold water. The mixed gases may now be conducted, by means of short rubber connections, through two tubes successively, each about 18 inches long, $\frac{1}{2}$ inch in diameter, and drawn out at the extremities. When it is judged that the air has been wholly expelled, of which an indication may be obtained by collecting the gas which escapes from the end of the second tube and observing its

Fig. 60.



colour, both tubes are detached, and their ends closed by means of stoppers or caps made of short pieces of rubber tubing.

If, now, the end of one tube be dipped into water to which a little solution of potash, coloured blue by litmus, is added, and the stopper removed, the liquid will slowly rise in the tube till one-half of the gas has been absorbed, and the liquid which enters the tube becomes bleached. The gas absorbed is chlorine, the residual colourless unabsorbed gas is hydrogen, and may be recognised by its inflammability. Now, by the former experiment, it was shown that 2 volumes of hydrogen chloride gas yield 1 volume of hydrogen. This experiment teaches that this 1 volume of hydrogen is accompanied by 1 volume of chlorine. The two elements, therefore, combine together without condensation or contraction.

That the hydrogen and chlorine unite in equal volumes, and that the resulting hydrogen chloride occupies the same space, may further be shown by exposing the second tube to daylight for a short time till colourless. It will then be found upon opening the end under mercury, that no gas escapes, neither does mercury enter ; the volume is unchanged. The resulting gas is, of course, entirely soluble in water. The instantaneous combination of the two may be effected by exposing the tube to direct sunlight or to the light of burning magnesium. In this case the tube must be strong and the caps securely wired on, so as to resist the force of the explosion.

BROMINE.

Symbol, Br. Atomic weight, 80. Vapour-density, 80.

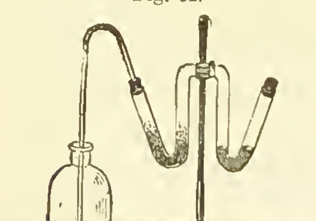
Bromine * was discovered by Balard in 1826. It is found in sea-water, and is a frequent constituent of saline springs, chiefly as magnesium bromide. A celebrated spring of the kind exists near Kreuznach, in Prussia. It is also obtained from the mother liquors of the salt at Stassfurth, and from some of the saline lakes in the United States.

Bromine is obtained by the following process :—The mother-liquor, from which the major part of the less soluble chlorides and sulphates have been removed by evaporation and crystallisation, is allowed to flow down a stoneware tower filled with stoneware balls, where it meets a stream of chlorine gas which decomposes the bromides present, liberating bromine. The resulting red vapour is condensed by passing it through a spiral stoneware pipe surrounded by cold water. The crude bromine is purified by distillation from a small quantity of potassium bromide, which exchanges bromine for any small quantities of chlorine retained by the liquid. The bromine passes over, in the form of a deep red vapour, together with water, and may be purified by redistillation.

Bromine is at common temperature a thin deep red very volatile liquid, which freezes at about $-24{\cdot}5^\circ$ and boils at 63°. The density of the liquid is 2·976, and that of the vapour 5·53 compared with air, and 80 compared with hydrogen. The odour of bromine is very suffocating and offensive, much resembling that of iodine, but more disagreeable. It is slightly soluble in water, more freely in alcohol, and most abundantly in ether. The aqueous solution bleaches, though less rapidly than that of chlorine.

Hydrogen Bromide, or **Hydrobromic Acid,** HBr.—This compound is obtained as a colourless fuming gas, together with phosphoric acid, by the action of water on bromine and phosphorus: $P + 5Br + 4H_2O = 5HBr + H_3PO_4$. The action of bromine upon phosphorus is very violent, and consequently great caution must be exercised in bringing them into contact. The preparation of hydrobromic acid gas may be readily effected on a small scale by the arrangement indicated in the accompanying figure.

Fig. 61.



One arm of the W-shaped tube is filled with broken glass, mixed with a few small pieces of phosphorus moistened with water, and is fitted with a tube for carrying off the gas. The other arm is closed by a cork after pouring into the bend 1 or 2

* From βρῶμος, a noisome smell.

cubic centimetres of bromine. On gently warming the latter the vapour of bromine passes through the phosphorus, and water being present, produces hydrogen bromide.

Hydrogen bromide cannot be procured free from bromine by the action of sulphuric acid upon a bromide, in consequence of the reduction of the sulphuric acid by the hydrogen bromide produced. Thus—

$$2HBr + H_2SO_4 = Br_2 + 2H_2O + SO_2.$$

Phosphoric acid may, however, be used.

When larger quantities of hydrogen bromide are required, a very convenient method consists in adding 1 molecular proportion of bromine, Br_2, drop by drop, to turpentine oil, $C_{10}H_{16}$, contained in a flask, and then applying heat to the product.

Hydrogen bromide closely resembles hydrogen chloride in composition and in chemical properties. The aqueous acid may be prepared by passing the gas into water, or directly by passing hydrogen sulphide through bromine water, $SH_2 + Br_2 = 2BrH + S$. It is colourless, has a pungent odour, an acid taste and reaction, and when saturated at 0°, a density of 1·78. By distillation the weak aqueous acid becomes stronger and the strong acid weaker, till an acid containing from 47·38 to 49·86 per cent. HBr passes over, under a pressure of 752 to 762 millimetres of mercury.

Chlorine and Bromine.—When chlorine gas is passed into liquid bromine, the two elements combine, forming a reddish-yellow mobile, volatile liquid, BrCl, which dissolves with yellow colour in water, the solution, when cooled below 0°, depositing a crystalline hydrate which melts at +7°.

IODINE.

Symbol, I. Atomic weight, 127. Vapour-density, 127.

This element was first noticed in 1812 by Courtois, a saltpetre manufacturer in Paris. Minute traces are found in combination with sodium or potassium in sea-water, and occasionally a much larger proportion in the water of certain mineral springs. It seems to be in some way beneficial to many marine plants, as these latter have the power of abstracting it from the surrounding water, and accumulating it in their tissues. It is from this source that all the iodine of commerce was formerly derived. It has been found in minute quantity in some aluminous slates of Sweden, and in several varieties of coal and turf. It occurs in combination with silver in some of the South American and Mexican silver ores. It is also found associated with some kinds of rock salt and in the sodium nitrate of Chili. The latter now forms the most important source of the iodine of commerce.

Kelp, or the half-vitrified ashes of sea-weed, was formerly made by the inhabitants of the Western Islands and the northern shores of Scotland and Ireland; but the production of kelp is now much reduced. A solution of this substance, evaporated to a small volume, yields sodium chloride, sodium carbonate, potassium chloride, and other salts which are removed as they successively crystallise. The dark brown mother-liquor left contains very nearly the whole of the iodine, as iodide of sodium, magnesium, etc.: this is mixed with sulphuric acid and manganese dioxide, and gently heated in a leaden retort, when the iodine distils over and condenses in the receiver. The theory of the operation is exactly similar to that of the preparation of chlorine; in practice, however, it requires careful management, in order to avoid the simultaneous liberation of chlorine and bromine.

$$MnO_2 + 2KI + 2H_2SO_4 = 2H_2O + K_2SO_4 + MnSO_4 + I_2.$$

The manganese is not absolutely necessary: potassium or sodium iodide, heated with an excess of sulphuric acid, evolves iodine. This effect is due to a secondary action between the hydriodic acid first produced and the excess of the sulphuric acid, in which both suffer decomposition, yielding iodine, water, and sulphurous acid.

The extraction of iodine from *caliche*, the crude sodium nitrate of Peru and Chili, involves the employment of different agents, because the element exists in this substance, not in the form of an iodide, but as an oxidised compound, an iodate. After the sodium nitrate has been dissolved in water, and the solution concentrated so as to cause the crystallisation of the nitrate, the mother-liquors retaining the iodate are mixed with an acid solution of sodium sulphite which precipitates the iodine—

$$Na_2I_2O_6 + 2NaHSO_3 + 3Na_2SO_3 = I_2 + 5Na_2SO_4 + H_2O.$$

The product from either source is purified by sublimation, either alone or mixed with a little potassium iodide, which retains any adhering chlorine or bromine.

Iodine crystallises in plates or scales of a bluish-black colour and imperfect metallic lustre resembling that of graphite; the crystals are sometimes very large and brilliant. Its density is 4·948. It melts between 113° and 115°, solidifies at 113·6°, and boils above 200°, the vapour having a beautiful violet colour.* It is slowly volatile also at common temperatures, and exhales an odour resembling that of chlorine. The density of the vapour is, by experiment, 8·716 compared with air, or 125·8 compared with hydrogen, the theoretical density being 126·53. At temperatures much above 700°, that is, at a bright-red heat, the density has been found to be considerably less. Iodine is almost insoluble in water; in alcohol it is much more freely soluble. Solutions of hydriodic acid and the iodides of the alkali-metals also dissolve it in large quantity: these solutions possess a brown colour. Carbon disulphide, chloroform, and benzene

* Whence the name, from ἰώδης, violet-coloured.

also dissolve iodine freely, producing liquids of a violet or red colour, especially when dilute.

Iodine stains the skin, but not permanently; it has a very energetic action upon the animal system, and is much used in medicine.

One of the most characteristic properties of iodine is the production of a splendid blue substance by contact with starch. The iodine for this purpose must be free or uncombined. It is easy, however, to make the test available for the purpose of recognising the presence of the element in question when a soluble iodide is suspected; it is only necessary to add a very small quantity of chlorine water, when the iodine, being displaced from combination, becomes capable of acting upon the starch.

Experiments.—1. Place about a quarter of an ounce of iodide of potassium in a small glass retort, add an equal weight of manganese dioxide and then sufficient dilute sulphuric acid to cover the powder. Apply a gentle heat and collect the vapour which is evolved in a small flask into the mouth of which the neck of the retort may be inserted. Observe the purple colour of the vapour and the black crystals which result from its condensation.

2. Place a crystal of iodine in a test-tube and cover it with water. Shake it, and observe that the iodine does not dissolve and the water is scarcely tinged. Now drop into the water a crystal of iodide of potassium, and leave the whole at rest for a few minutes. A deep brown solution of potassium tri-iodide forms at the bottom, and on shaking up mixes with the rest of the water.

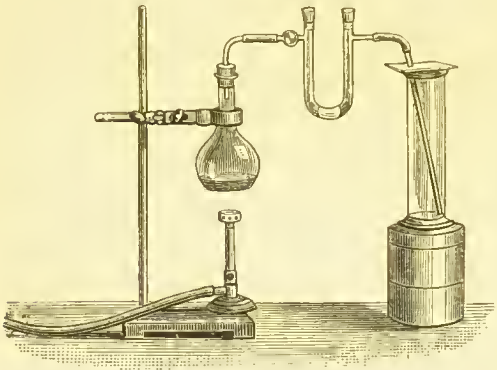
3. Take a pinch of white starch, shake it up with a teaspoonful of cold water, then pour upon it a test-tubeful of boiling water. Boil the mixture for a few minutes and let it cool. To a portion of this contained in a test-tube add one drop of the solution made in experiment 2. An intensely deep blue liquid and precipitate result. To another portion of starch liquor add a drop of solution of potassium iodide. No colour results. Now add a drop of chlorine water or of bromine water. The blue colour indicating free iodine is at once developed.

Iodine, in the presence of water, acts in some cases as an oxidising agent, but its powers in this respect are greatly inferior to those of chlorine and bromine, and consequently it has scarcely any bleaching action upon organic colouring matters.

Hydrogen Iodide, or **Hydriodic Acid**, HI.—The simplest process for preparing hydrogen iodide gas is to introduce into a small flask a few grams of red phosphorus with sufficient water to cover it. Iodine is added in portions of about half a gram, allowing time for the reaction to become complete before adding more. When the liquid begins to emit colourless fumes, the flask may be attached to a small U-shaped tube (see fig. 62) containing a little red phosphorus, through which the gas evolved on application of heat to the flask is made to pass. The gas is very dense, and may be collected in dry bottles by displacement of air.

Hydrogen iodide gas resembles the corresponding chlorine compound; it is colourless, and highly acid, fumes in the air, and is very soluble in water. Its density is 4·3737 compared with air, or 64 compared with hydrogen. By weight, it is composed of 127 parts iodine and 1 part hydrogen; and by measure of equal volumes of iodine vapour and hydrogen united without condensation. Hydrogen iodide differs from both hydrogen chloride and bromide in the fact that it is very easily decomposed by heat. On plunging a heated wire into a jar full of the gas, purple fumes of iodine are immediately produced.

Fig. 62.



Solution of hydriodic acid, if not required very strong, may be prepared by a process much less troublesome than the above. Iodine in fine powder is suspended in water, and a stream of washed hydrogen sulphide is passed through the mixture; sulphur is then deposited, and the iodine is converted into hydrogen iodide. The action ceases when the resulting solution acquires a density of 1·56, and contains about 48 per cent. of hydrogen iodide. When the liquid has become colourless, it is heated, to expel the excess of hydrogen sulphide, and filtered. The solution cannot be kept long, unless protected from the air, as the oxygen gradually decomposes the hydrogen iodide, and iodine is set free, which, dissolving in the remainder, colours it brown.

Iodine and Chlorine.—These bodies unite directly, forming a monochloride and a trichloride. The *monochloride*, ICl, is obtained by passing dry chlorine gas over iodine till the whole is liquefied, but no longer.

Iodine monochloride is a dense reddish-brown liquid, which slowly solidifies in black crystals which melt at 24° and boil at 101°; soluble in alcohol and ether; decomposed by water, with formation of hydrochloric and iodic acids, and separation of iodine. Sulphurous acid and hydrogen sulphide decompose it with separation of iodine; with aqueous solutions of alkalis, it yields a chloride and an iodate, together with free iodine; thus, with potash—

$$5ICl + 6KHO = 5KCl + KIO_3 + 3H_2O + 2I_2.$$

The *trichloride*, ICl_3, is produced by treating iodine at a gentle heat with chlorine in excess. It crystallises in orange-yellow

needles; melts at 20° to 25°, giving off chlorine, which it reabsorbs on cooling; acts on most other substances like the monochloride.

In contact with a small quantity of water it is partly resolved into iodic acid, hydrochloric acid, and the monochloride—

$$2ICl_3 + 3H_2O = 5HCl + ICl + HIO_3.$$

A large quantity of water dissolves it, probably as a mixture of hydrochloric and iodic acids containing free iodine—

$$5ICl_3 + 9H_2O = 15HCl + 3HIO_3 + I_2.$$

Iodine and Bromine.—Iodine unites with bromine, forming a volatile crystalline compound, IBr, and a dark liquid, probably IBr_5.

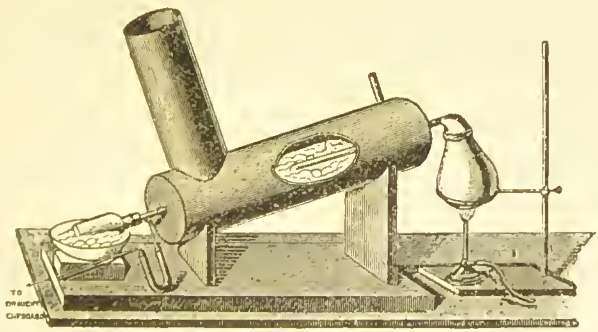
Iodine and Fluorine.—The pentafluoride IF_5 is described as a colourless, fuming liquid.

FLUORINE.

Symbol, F. Atomic weight, 19. Density, 19.

This element exists in considerable quantity, in combination with calcium, forming the mineral called fluorspar, CaF_2, which crystallises in fine cubes of various colours, and with sodium and aluminium in the mineral cryolite, Na_3AlF_6. Fluorine occurs also in

Fig. 63.



small quantity as a constituent of bones and other animal substances. Its intense affinities for metals and for silicon, which is a constituent of glass, have baffled many attempts to obtain it in a state fit for examination, but, in 1886, it was at last definitely isolated by Moissan. His process consists in first preparing pure anhydrous hydrogen fluoride by the action of heat upon the double fluoride KF.HF. This salt, thoroughly dried, is placed in a platinum alembic connected with a bent tube surrounded by ice (see fig. 63);

on applying heat the salt is decomposed; hydrogen fluoride distils over, and potassium fluoride remains behind. The liquid thus obtained boils at 19·5° and is very corrosive, and, on this account, dangerous. When quite free from water it resists the passage of an electric current, but if a small quantity of potassium fluoride is added it yields hydrogen and fluorine. The experiment is conducted in a tube of platinum with stoppers of fluorspar (fig. 64), the electrodes being formed of rods of platinum alloyed with iridium. The liquid during the passage of the current becomes much heated, and the tube must be surrounded by a cooling agent, the most convenient being methyl chloride, which boils at −27°.

Fig. 64.

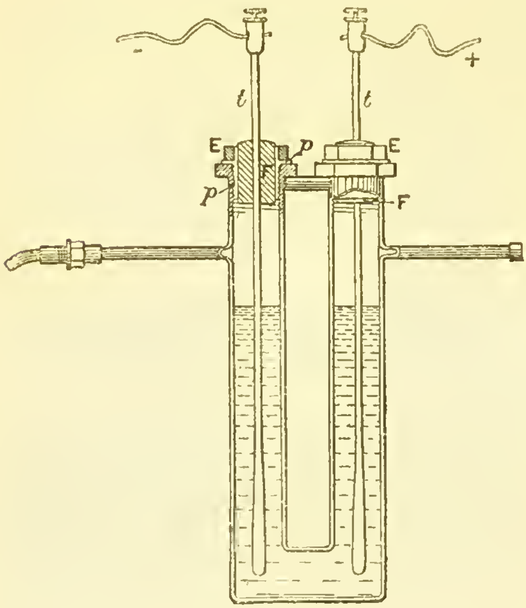


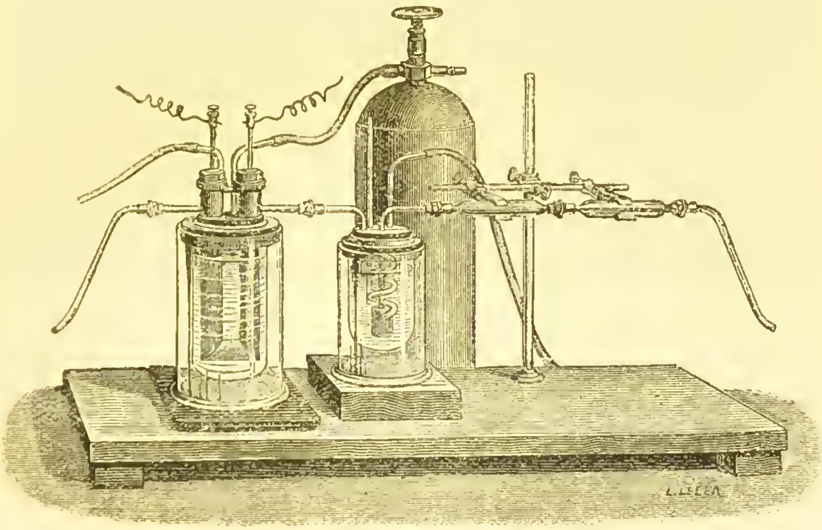
Figure 65 shows the disposition of the apparatus. On leaving the U-tube, the gaseous fluorine passes first through a spiral platinum tube, also cooled by methyl chloride, and then through one or two platinum tubes charged with pieces of fused sodium fluoride; the object of both being to remove any accompanying hydrogen fluoride. A supply of the liquid methyl chloride used as a refrigerating agent is contained in the copper or steel cylinder shown at the back. Hydrogen gas escapes from the other branch of the U-tube.

Fluorine is a pale green gas, which has a very powerful action upon nearly all substances. Crystallised silicon and boron ignite in it, forming gaseous fluorides. Arsenic, antimony, sulphur, iodine, also burn, but metals are less readily attacked, owing probably to the formation of a protecting crust of solid fluoride. Fluorine mixed with hydrogen detonates violently, and it decomposes water, forming hydrofluoric acid and ozone. It also decomposes chlorides such as common salt, liberating chlorine. Organic bodies such as cork, alcohol, and oils, are violently attacked and inflamed.

Hydrogen Fluoride, or Hydrofluoric Acid, HF.—When powdered calcium fluoride is heated with concentrated sulphuric acid in a retort of platinum or lead connected with a carefully cooled

receiver of the same metal, a very volatile colourless liquid is obtained, which emits copious white and highly suffocating fumes in the air. This is the anhydrous acid, not however quite pure. It may be obtained in a state of perfect purity by distilling hydrogen-potassium fluoride, HF,KF, by heating the salt in a platinum retort, the condenser of which is surrounded by a freezing mixture of ice and salt, or ice and calcium chloride, which gives a temperature of $-25°$, the receiver being immersed in a similar mixture, as already shown in figure 63. As thus prepared, it is at ordinary temperatures a colourless, transparent, mobile liquid, having a density of 0·9879 at 12·8°,

Fig. 65.



extremely volatile, boiling at 19·4°, fuming densely at ordinary temperatures, and absorbing water greedily from the air.

Gore showed, that when anhydrous fluoride of silver is heated with hydrogen, 1 volume of the gas in uniting with fluorine produces approximately 2 volumes of hydrogen fluoride, if measured at about 100° C., though the volume was considerably less at lower temperatures. Mallet and Thorpe at different times have also determined the density of the vapour of hydrogen fluoride, and have shown that at temperatures not much above its boiling point, the density exceeds the value required by the formula HF. But according to Thorpe, the vapour attains the normal density 10, corresponding to the molecular weight $20 = 1 + 19$, at about 88° under normal pressure.

When hydrogen fluoride is put into water, it unites with the latter with great violence; the dilute solution attacks glass very easily, though, according to Gore, the dry acid has no action upon glass. The concentrated acid, dropped upon the skin, occasions deep malignant ulcers, so that great care is requisite in its management.

In a diluted state, this acid is occasionally used in the analysis of siliceous minerals, when alkali is to be estimated. It is employed also for etching on glass, for which purpose the acid may be prepared in vessels of lead, that metal being but slowly attacked under these circumstances. The vapour of the acid is also very advantageously applied to the same purpose in the following manner:—The glass to be engraved is coated with etching-ground or wax, and the design traced in the usual way with a pointed instrument, or by a stencil plate. A shallow basin, made by beating up a piece of sheet-lead, is then prepared, a little powdered fluorspar placed in it, and enough sulphuric acid added to form with the latter a thin paste. The glass is placed upon the basin, with the waxed side downwards, and gentle heat applied beneath, which speedily disengages the vapour of hydrofluoric acid. In a very few minutes the operation is complete; the glass is then removed, and cleaned by a little warm oil of turpentine. When the experiment is successful, the lines are very clean and smooth.

OXIDES AND OXY-ACIDS OF CHLORINE.

There are four oxyacids of chlorine, the composition of which is as follows:—

	Formula.	Composition by weight. Hydrogen.		Chlorine.		Oxygen.
Hypochlorous acid, .	$HClO$	1	+	35·4	+	16
Chlorous acid, . .	$HClO_2$	1	+	35·4	+	32
Chloric acid, . .	$HClO_3$	1	+	35·4	+	48
Perchloric acid, . .	$HClO_4$	1	+	35·4	+	64

The following anhydrous oxides are also known:—

	Chlorine.		Oxygen.
Chlorine monoxide, or Hypochlorous oxide, Cl_2O	35·4	+	16
Chlorine peroxide, ClO_2 . . .	35·4	+	32

The oxides corresponding with chloric and perchloric acid have not been obtained.

Hypochlorous and chloric acids are produced by the action of chlorine on certain metallic oxides in presence of water; hypochlorous and chlorous acids also by direct oxidation of hydrochloric acid. Perchloric acid and chlorine peroxide result from the decomposition of chloric acid.

Hypochlorous Oxide, Acid, and Salts.—The oxide is best prepared by the action of chlorine gas upon dry mercuric oxide. This oxide, prepared by precipitation, and dried by exposure to a strong heat, is introduced into a glass tube kept cool, and well-washed dry chlorine gas is slowly passed over it. Mercuric chloride ($HgCl_2$) and hypochlorous oxide are thereby formed; the latter is collected

by displacement of air. The reaction by which it is produced is represented by the equation,

$$HgO + 2Cl_2 = Cl_2O + HgCl_2.$$

The mercuric chloride, however, combines with another portion of the oxide when the latter is in excess, forming a peculiar brown compound, an oxychloride of mercury, $HgCl_2,HgO$. The *crystalline* mercuric oxide prepared by calcining the nitrate, or by the direct oxidation of the metal, is scarcely acted upon by chlorine under the circumstances described.

Hypochlorous oxide is a pale yellow gaseous body of peculiar odour, containing, in every two measures, two measures of chlorine and one of oxygen, and is therefore analogous in constitution to water. The gas condenses by cold to a red liquid which boils at about $-17°$. Both the gas and the liquid are violently explosible by heat, or even, in the case of the liquid, upon agitation.

Hypochlorous acid is formed by the solution of hypochlorous oxide in water, but is more conveniently produced by decomposing a metallic hypochlorite with carbonic acid. It is also readily made by passing chlorine gas into water holding mercuric oxide or calcium carbonate (chalk), $CaCO_3$, in suspension. The products in the latter case are carbon dioxide, calcium chloride, and hypochlorous acid :

$$CaCO_3 + H_2O + 2Cl_2 = CO_2 + CaCl_2 + 2HClO.$$

The aqueous solution of hypochlorous acid has a yellowish colour, an acid taste, and a characteristic sweetish smell. The strong acid decomposes rapidly even when kept in ice. The dilute acid is more stable, but is decomposed by long boiling into chloric acid, water, chlorine, and oxygen. Hydrochloric acid decomposes it, with formation of chlorine :

$$HClO + HCl = H_2O + Cl_2.$$

It is a very powerful bleaching and oxidising agent, converting many of the elements—iodine, selenion, and arsenic, for example—into their highest oxides, and at the same time liberating chlorine.

Metallic hypochlorites may be obtained in the pure state by neutralising hypochlorous acid with metallic hydroxides, such as those of sodium, calcium, copper, etc. ; but they are usually prepared by passing chlorine gas into cold solutions of alkalis or alkaline carbonates, or over the dry hydroxides of the earth-metals. In this process a metallic chloride is formed at the same time. With dry slaked lime, for example, which is a hydroxide of calcium, CaH_2O_2, the products are calcium hypochlorite, $CaCl_2O_2$, calcium chloride, and water :

$$2CaH_2O_2 + 2Cl_2 = CaCl_2O_2 + CaCl_2 + 2H_2O.$$

The salts thus obtained constitute the bleaching and disinfecting salts of commerce. They will be more fully described under the head of Calcium Salts.

Chlorous Acid, $HClO_2$, **and Chlorites.**—When chlorine peroxide is dissolved in water, the solution is supposed to contain chlorous and chloric acids. Similarly when the peroxide is absorbed by an alkaline solution, a chlorite and chlorate are said to be formed. The chlorites are, however, very unstable substances, and have been very imperfectly investigated.

Chlorine Peroxide, ClO_2.—When potassium chlorate is made into a paste with concentrated sulphuric acid, and cooled, and this paste is very cautiously heated by warm water in a small glass retort, this compound, in the form of a deep yellow gas, is evolved. It can be collected only by displacement, since mercury decomposes and water absorbs it.

Chlorine peroxide has a powerful odour, quite different from that of the preceding compounds, and of chlorine itself. The gas is also exceedingly explosive, being resolved with violence into its elements by a temperature short of the boiling point of water. Its preparation is, therefore, always attended with danger, and should be performed only on a small scale. It is composed by measure of 1 volume of chlorine and 2 volumes of oxygen, condensed into 2 volumes. The gas is condensable by cold to a reddish liquid which boils at about 10°, and is fearfully explosive. Its vapour-density at 10·7° and 718 mm. is 34·5. Hence its molecular formula is ClO_2. The solution of the gas in water bleaches.

The *euchlorine* of Davy, prepared by gently heating potassium chlorate with hydrochloric acid, is a mixture of chlorine peroxide and free chlorine. This mixture, which forms a very powerful oxidising agent, is often used in analysis.

The production of chlorine peroxide from potassium chlorate and sulphuric acid depends upon the spontaneous splitting of the chloric acid into chlorine peroxide and perchloric acid, which latter remains as a potassium salt.

$$\underset{\text{Potassium chlorate.}}{6KClO_3} + \underset{\text{Hydrogen sulphate.}}{3H_2SO_4} = \underset{\text{Chloric oxide.}}{4ClO_2} + \underset{\text{Hydrogen perchlorate.}}{2HClO_4} + \underset{\text{Potassium sulphate.}}{3K_2SO_4} + \underset{\text{Water.}}{2H_2O}.$$

When a mixture of potassium chlorate and sugar is touched with a drop of oil of vitriol, it is instantly set on fire, the chlorine tetroxide disengaged being decomposed by the combustible substance with such violence as to cause ignition. If crystals of potassium chlorate be thrown into a glass of water, a few small fragments of phosphorus added, and then oil of vitriol poured down a narrow funnel reaching to the bottom of the glass, the phosphorus will burn beneath the surface of the water, by the assistance of the oxygen of the chlorine peroxide disengaged. The liquid at the same time becomes yellow, and acquires the odour of that gas.

Chloric Acid, $HClO_3$.—This is the most important compound of the series. When chlorine is passed to saturation into a moderately strong hot solution of potassium hydroxide or carbonate, and the

liquid concentrated by evaporation, it yields, on cooling, thin prismatic crystals of a colourless salt, consisting of potassium chlorate. The mother-liquor contains potassium chloride :

$$\underset{\text{Potassium hydroxide.}}{6KHO} + \underset{\text{Chlorine.}}{3Cl_2} = \underset{\text{Potassium chloride.}}{5KCl} + \underset{\text{Potassium chlorate.}}{KClO_3} + \underset{\text{Water.}}{3H_2O}.$$

From potassium chlorate, chloric acid may be obtained by boiling the salt with a solution of hydrofluosilicic acid, which forms an almost insoluble potassium salt, decanting the clear liquid, and digesting it with a little silica, which removes the excess of the hydrofluosilicic acid. Or barium chlorate dissolved in water is mixed with exactly sufficient dilute sulphuric acid to precipitate the whole of the barium. The liquid may be poured off clear after subsidence of the precipitated barium sulphate.

$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4 + 2HClO_3.$$

Filtration through paper must be avoided.

By cautious evaporation, the acid may be so far concentrated as to assume a syrupy consistence ; it is then very easily decomposed. It sometimes sets fire to paper, or other dry organic matter, in consequence of the facility with which it is deoxidised by combustible bodies.

The chlorates are easily recognised ; they give no precipitate when in solution with silver nitrate ; they evolve pure oxygen when heated, passing thereby into chlorides : and they afford when treated with sulphuric acid, the characteristic explosive yellow gas already described. The dilute solution of the acid has no bleaching power.

The most important chlorate is the potassium salt which will be described in connection with that metal.

Perchloric Acid, $HClO_4$.—Potassium perchlorate is easily prepared by heating potassium chlorate to fusion until the melted salt begins to become pasty. On dissolving the solidified mass in boiling water, and allowing the solution to cool, the perchlorate is deposited in granular crystals, whilst potassium chloride remains in solution,

$$(x + y)(KClO_3) = xKClO_4 + yKCl + (3y - x)O.$$

Perchloric acid is obtained by distilling potassium perchlorate with sulphuric acid. Pure perchloric acid is a colourless liquid, of density 1·782 at 15·5°, not solidifying at −35° ; it soon becomes coloured from liberation of chlorine. The vapour of perchloric acid is transparent and colourless ; in contact with moist air it produces dense white fumes. The acid, when cautiously mixed with a small quantity of water, solidifies to a crystalline mass, which is a compound of perchloric acid with one molecule of water, $HClO_4 + H_2O$. When brought into contact with carbon, ether, or other inflammable substances, perchloric acid explodes with great violence.

OXY-ACIDS OF BROMINE.

Hypobromous Acid, HBrO, is formed by agitating bromine-water with mercuric oxide, according to the equation :

$$HgO + 2Br_2 + H_2O = HgBr_2 + 2HOBr.$$

The greater part of the hypobromous acid contained in the resulting solution is resolved on distillation into bromine and oxygen, but the acid may be distilled in a vacuum at 40°, without decomposition. Aqueous hypobromous acid is a light straw-yellow liquid, which resembles hypochlorous acid in its properties, is a powerful oxidising agent, and bleaches vegetable colours.

Hypobromites are formed by adding bromine to solutions of alkali or of alkaline earth, avoiding rise of temperature.

Bromic Acid, $HBrO_3$.—Caustic alkalis react with bromine, in the same manner as with chlorine, yielding a bromide and bromate, which may be separated by the inferior solubility of the latter. Bromic acid, obtained from barium bromate, closely resembles chloric acid, and is very unstable. The bromates when heated give off oxygen, and are converted into bromides.

Perbromic Acid, $HBrO_4$, is unknown.

No anhydrous oxide of bromine has yet been obtained.

OXIDES AND OXY-ACIDS OF IODINE.

Iodine Pent-Oxide, I_2O_5, and **Iodic Acid,** HIO_3.—Iodic acid may be prepared by boiling iodine with absolute nitric acid of density 1·5. After several hours the iodine dissolves, and on evaporating the solution to dryness a white residue remains which may be dissolved in water and crystallised. This is iodic acid HIO_3. The same compound may be obtained by allowing chlorine to act upon powdered iodine in the presence of water. In this case probably the first product is the trichloride ICl_3 which is then decomposed by water (p. 107.) The ultimate effect may be expressed by the equation,

$$I_2 + 5Cl_2 + 6H_2O = 10HCl + 2HIO_3.$$

Iodic acid is a very soluble substance, crystallising in colourless six-sided tables. At 170° it is resolved into water and the pent-oxide which forms tabular rhombic crystals, and when heated to a higher temperature is completely resolved into iodine and oxygen. The solution of iodic acid is readily deoxidised by sulphurous acid. The iodates differ in some respects from the chlorates : that of potassium is decomposed by heat into potassium iodide and oxygen gas.

Potassium iodate, along with iodide, is formed when iodine is added to solution of caustic potash,

$$6KHO + 3I_2 = 5KI + KIO_3 + 3H_2O.$$

It is perhaps best prepared by boiling potassium chlorate with iodine and a small quantity of nitric acid. The action probably consists in the formation of successive portions of chloric acid by the action of the nitric acid, and this in turn exchanges its chlorine for iodine. Chlorine gas escapes.

$$HClO_3 + I_2 = HIO_3 + ICl$$

and

$$HClO_3 + ICl = HIO_3 + Cl_2.$$

Iodic acid contains only one atom of hydrogen exchangeable for metals. Hence the formula of the normal iodate of potassium for example is KIO_3. But it differs from the corresponding chlorate and bromate by forming definite compounds with the acid,

$$KIO_3.HIO_3 \quad \text{and} \quad KIO_3.2HIO_3.$$

Hydrogen Periodate, or Periodic Acid, H_5IO_6 or $H_2IH_3O_6$.—When solution of sodium iodate is mixed with caustic soda, and a current of chlorine is passed through the liquid, two salts are formed—namely, sodium chloride and a sparingly soluble sodium periodate, $Na_2H_3IO_6$, the reaction taking place as represented by the equation—

$$Na_2I_2O_6 + 6NaHO + 2Cl_2 = 4NaCl + 2Na_2H_3IO_6.$$

This sodium salt is separated, converted into a silver salt, and dissolved in nitric acid: the solution yields, on evaporation, crystals of yellow silver periodate, $Ag_2IH_3O_6$, from which the acid may be separated by the action of water, which resolves the salt into free acid and an insoluble periodate, Ag_5IO_6.

Periodic acid crystallises from its aqueous solution in deliquescent oblique rhombic prisms, which melt at 133°, and are resolved at 140° into oxygen, water, and iodine pent-oxide. Although periodic acid contains six atoms of hydrogen, two only are usually replaceable by metals, and the acid is regarded as dibasic.

The composition of the silver salt just mentioned, shows that the periodates are somewhat complicated in constitution. The several series of known salts may, however, be supposed to be made up of the elements of the hypothetical heptoxide with different proportions of the metallic oxide. Thus the principal silver salts may be expressed as follows:

Ortho-periodate.

$$I_2O_7 + 5Ag_2O = 2Ag_5IO_6.$$

Meso-periodate.

$$I_2O_7 + 2Ag_2O + H_2O = 2Ag_2IHO_5.$$

Meta-periodate.

$$I_2O_7 + Ag_2O = 2AgIO_4.$$

The solution of periodic acid is reduced by many organic substances, and instantly by hydrochloric acid, sulphurous acid, and hydrogen sulphide. With hydrochloric acid it forms water, iodine chloride, and free chlorine. The metallic periodates are resolved by heat into oxygen and metallic iodides.

THE SULPHUR GROUP OF ELEMENTS.

THE three elements, sulphur, selenion, and tellurium, of which an account now follows, closely resemble one another in physical and in chemical characteristics. They are solid, brittle, fusible, and volatile substances, which readily burn, when ignited, in air or oxygen, giving rise to an oxide or mixture of oxides, which is also easily volatile or even gaseous at common temperatures. Their oxides united with water produce very strong acids. Their chief compounds with hydrogen are gases possessing a fœtid odour, and contain their own volume of hydrogen.

These elements exhibit the same kind of relationship among their atomic weights which has already been indicated in connection with the halogen group; that is, when ranged in the order of their chemical activity, the middle term of the series, selenion in the present case, has an atomic weight nearly equal to the arithmetical mean of the atomic weight of the other two. Thus :—

	Atomic Weight.	Mean of Extremes.
Sulphur, ...	32	...
Selenion, ...	79	79
Tellurium, . . .	126 (approx.)	...

When the characters of the metals come to be discussed, it will also be observed that in this series the high atomic weight of tellurium is connected with the semi-metallic characters exhibited by that element.

SULPHUR.

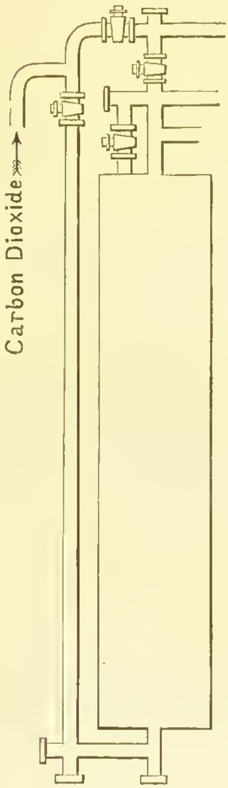
Symbol, S. Atomic weight, 32. Vapour-density at a red heat, 32.

Sulphur occurs abundantly in nature both free and in combination. In the free state it is found in the neighbourhood of volcanos, both active and extinct, either in transparent yellow crystals, or in opaque crystalline masses, and is separated from the rock or earth in which it is imbedded, by setting fire to heaps of the material, and collecting those portions which escape combustion and run out in a melted state at the bottom of the pile. Large quantities of sulphur are thus obtained from Italy and Sicily.

Sulphur occurs, however, in still greater abundance in combination with metals forming the *metallic sulphides*, *e.g.*, iron pyrites, FeS_2, copper pyrites, $CuFeS_2$, galena, PbS, cinnabar, HgS ; or with

metals and oxygen, forming *sulphates*, *e.g.*, gypsum, $CaSO_4.2H_2O$, heavy spar, $BaSO_4$, Epsom salt, $MgSO_4.7H_2O$, etc.

Fig. 66.



Some quantities of sulphur are obtained by the roasting of pyrites containing iron and copper. Smaller quantities are obtained as a bye-product in the manufacture of coal gas. The gas, as it issues from the retorts, contains hydrogen sulphide, and by passing it over oxide of iron, a sulphide of iron is formed, which on exposure to the air, is oxidised, with separation of sulphur: $2FeS + O_3 = Fe_2O_3 + S_2$.

Sulphur is also obtained from the residue or waste of the soda-manufacture (see SODIUM), which consists of calcium sulphide mixed with chalk, lime, and alkaline sulphides. The accumulated masses of this mixture exposed to the air absorb oxygen; the calcium sulphide is partly oxidised to thiosulphate, CaS_2O_3, and a polysulphide, CaS_5, both of which are soluble in water, whilst the monosulphide, CaS, is almost insoluble. After dissolving out the soluble constituents of the mass by water, the addition of hydrochloric acid to the liquid causes the precipitation of most of the sulphur, thus:—

$$2CaS_5 + Ca_2S_2O_3 + 6HCl = CaCl_2 + 12S + 3H_2O.$$

Another more important process which enables the manufacturer to avoid the accumulation of the waste, and provide an abundant supply of sulphur, has been patented by Messrs Chance of Birmingham. The fresh waste is suspended in water and placed in a series of vertical iron cylinders, of which one is shown in fig. 66, into which carbon dioxide, accompanied by atmospheric nitrogen, obtained from a lime-kiln, is pumped. Hydrogen sulphide gas disengaged in the first vessel,

$$CaS + H_2O + CO_2 = CaCO_3 + H_2S,$$

is driven into the vessels connected with it and is there absorbed, producing calcium hydrosulphide,

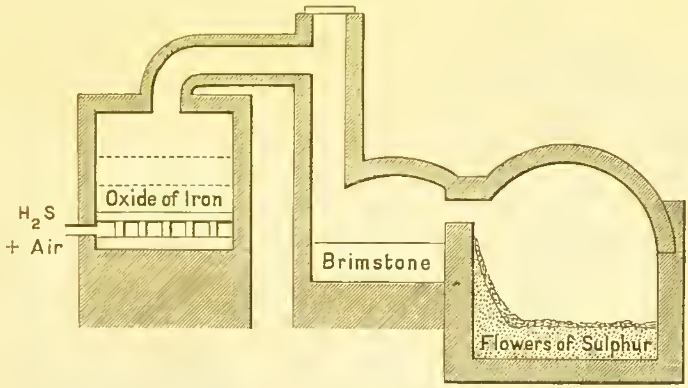
$$CaS + H_2S = Ca(HS)_2.$$

This, in its turn, is decomposed by the carbonic acid, and a gas containing a large proportion of sulphuretted hydrogen is evolved. The gas thus produced may be stored in a gas-holder, and subsequently employed in the manufacture of sulphuric acid. When the object is to obtain sulphur, the gas is conducted into a brick chamber (fig. 67) containing a quantity of peroxide of iron. Air admitted at the same

time in suitable proportion, causes the oxidation of the hydrogen and the liberation of sulphur, which, being vaporised by the heat of the reaction, is collected in a series of cooling chambers, partly in the form of a fine crystalline dust (flowers of sulphur), partly in the molten state, from which it may be cast into moulds in any desired form.

Properties.—Pure sulphur is a pale-yellow brittle solid, of well-known appearance. It melts when heated, and distils over unaltered, if air be excluded. The crystals of sulphur exhibit two distinct and incompatible forms—namely, first, an octahedron belonging to the rhombic system (fig. 68), which is the figure of native sulphur, and of sulphur deposited at common temperatures from solution in carbon bisulphide; and, secondly, a lengthened monoclinic prism, the primary form of which is shown in fig. 69, the form assumed

Fig. 67.



when a mass of sulphur is melted, and, after partial cooling, the crust on the surface is broken, and the fluid portion poured out. Fig. 70 shows the result of such an experiment.

The density of sulphur varies according to the form in which it is crystallised. The octahedral variety has the density 2·045 at 4·5°; the prismatic variety has the density 1·96.

Sulphur melts at 114·5°, forming a thin amber-coloured liquid; when further heated, it begins to thicken, and acquires a deeper colour; and between 221° and 249° it is so tenacious that the vessel in which it is contained may be inverted for a moment without the loss of its contents. Heated somewhat beyond this temperature, it again liquefies, though never becoming so fluid as at first. If in this state it be suddenly cooled by pouring into water, it retains for many hours a remarkably tough and plastic condition. After a while it again becomes brittle and crystalline. From the temperature last-mentioned to the boiling point—about 448°—sulphur again becomes thin and liquid. In the preparation of commercial flowers of sulphur, the vapour is conducted into a large cold chamber, where it condenses in minute crystals.

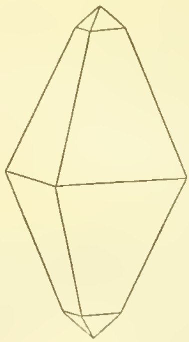
The density of sulphur vapour, referred to that of air as unity, is represented by the following numbers (Biltz):—

Temperature,	467·9°	501·7°	534·4°	606°
Density .	7·937	7·015	6·975	4·734

At 800° to 1000° the density is 2·22 compared with air or 31·98 compared with hydrogen taken as unity (Deville).

Sulphur is insoluble in water and alcohol; oil of turpentine and the fat oils dissolve it, but the best substance for the purpose is

Fig. 68.



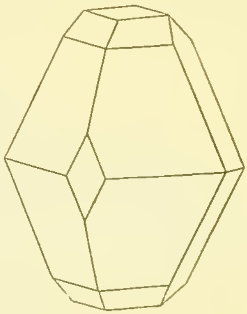


Fig. 69.

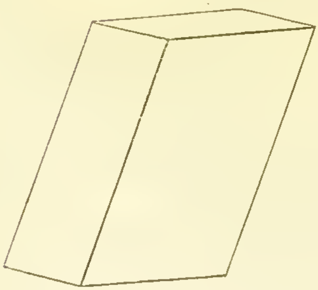


Fig. 70.

carbon bisulphide. In its chemical relations sulphur bears some resemblance to oxygen: to very many oxides there are corresponding sulphides, and the sulphides often unite among themselves, forming crystallisable compounds analogous to oxysalts, as in the following examples:—

Oxygen Compounds.	Sulphur Compounds.
K_2O	K_2S.
KHO	KHS.
CO_2	CS_2.
K_2CO_3	K_2CS_3.
K_2SO_4	$K_2S(SO_3)$.
K_3AsO_3	K_3AsS_3.

Sulphur has, however, a greater tendency to accumulate than oxygen, and it accordingly gives rise to many *poly*-sulphides, for which there are no correspondents among oxides, *e.g.*, K_2S_5, CaS_5, FeS_2, Fe_7S_8, etc.

The chief varieties of sulphur are as follows :—

1. Native sulphur or sulphur crystallised from carbon bisulphide at common temperatures, consisting wholly of the *octahedral* variety, entirely soluble in carbon bisulphide.

2. *Prismatic* sulphur formed by fusion and cooling; transformed into octahedral sulphur slowly by keeping or immediately on immersion in carbon bisulphide.

3. *Plastic* sulphur, obtained as already described; insoluble in carbon bisulphide.

4. Powdery *amorphous* sulphur precipitated during the decomposition of sulphur chlorides by water, and by the addition of acids to soluble thiosulphates. Insoluble in carbon bisulphide.

There are three chief commercial forms of sulphur, namely, *brimstone*, which occurs in blocks or rods of a yellow colour, consisting almost entirely of the octahedral variety; *flowers of sulphur*, also composed chiefly of the octahedral form, but usually containing a small quantity of a variety which is not dissolved by carbon bisulphide; and *milk of sulphur*, obtained by boiling common sulphur with lime and water, and adding excess of an acid to the yellow solution. The nearly white precipitate which results consists of a mixture of a variety soluble in carbon bisulphide with another which is insoluble in that menstruum. The former of these probably results from the decomposition of the polysulphide present in the solution; the latter is a product of the decomposition of the thiosulphate also formed by the interaction of the lime and sulphur. The changes which occur may be represented by these equations :—

$$3Ca(HO)_2 + 12S = CaS_2O_3 + 2CaS_5 + 3H_2O$$

and

$$CaS_2O_3 + 2CaS_5 + 6HCl = 3CaCl_2 + 3H_2O + 12S.$$

Experiments.—1. Place in a small dry flask about an ounce of carbon bisulphide. Add some flowers of sulphur, then gently heat the flask by dipping it into warm water, avoiding the approach of a flame. After a few minutes filter the solution through a small dry filter-paper into a beaker which should be covered, and set by in a draught chamber, so that the carbon bisulphide may very slowly evaporate away. In a few hours distinct octahedral crystals of sulphur will be formed.

2. Fill a two-ounce porcelain crucible with sulphur. Heat it gently till the whole is just melted, then allow it to cool. A crust soon forms upon the surface. Remove this with a knife, pour off the still liquid portion and examine the prismatic crystals which line the cup.

3. Crush one or two ounces of roll sulphur to coarse powder, place

in a dry flask, and heat gently over a lamp. Notice that the sulphur when just melted forms a clear and limpid liquid.

4. Apply a somewhat stronger heat, shaking the flask all the time. In a few minutes the liquid becomes suddenly changed into a gelatinous solid consisting of plastic sulphur.

5. Raise the temperature still further. The colour of the mass gets darker at the same time it becomes semifluid. Now pour a portion of it in a thin stream into a dish of cold water, and examine the resulting elastic threads.

6. Continue the application of heat till the sulphur boils, and the colour of the vapour may be observed.

Compounds of Sulphur and Hydrogen.

Hydrogen Monosulphide.—*Hydrosulphuric Acid*; *Sulphuretted Hydrogen*, H_2S.—Hydrogen sulphide occurs in volcanic gases, and the gases evolved from some mineral springs, as those at Harrogate. It is a frequent product of the putrefaction of animal matters.

Hydrogen sulphide may be formed by direct union of its elements, when hydrogen gas is passed through boiling sulphur, or more freely, when hydrogen and sulphur vapours are carried together through a red-hot tube, but for practical purposes there are only two methods by which this important compound can be readily prepared, namely, by the action of dilute sulphuric acid upon iron monosulphide, and by the decomposition of antimony trisulphide with hot hydrochloric acid. The first method yields it most easily, the second in the purest state.

Iron monosulphide may be put into an apparatus similar to that used for hydrogen (fig. 4, A, p. 23), together with water, and sulphuric acid added by the funnel. Hydrogen sulphide is then evolved, while ferrous sulphate remains in solution :—

$$FeS + H_2SO_4 = H_2S + FeSO_4.$$

By the other plan, finely powdered antimony trisulphide is put into a flask to which a cork and bent tube can be adapted, and strong liquid hydrochloric acid is poured upon it. On the application of heat, a double interchange occurs, hydrogen sulphide and antimony trichloride being formed. The action lasts only while the heat is maintained :—

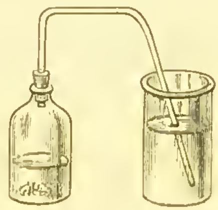
$$Sb_2S_3 + 6HCl = 3SH_2 + 2SbCl_3.$$

Hydrogen sulphide is a colourless gas, having the offensive odour of putrid eggs. It is not irritant, but, on the contrary, powerfully narcotic, and the continued inhalation of air containing only small quantities of it is decidedly injurious to health. When set on fire, it burns with a blue flame, producing sulphur dioxide, when the supply of air is abundant, and depositing sulphur when the oxygen

is deficient. Mixed with chlorine, it is instantly decomposed, with separation of the whole of the sulphur.

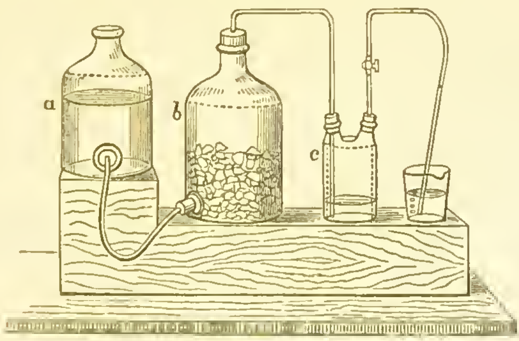
This gas has a density 1·171 referred to air, or 17 referred to hydrogen as unity; a litre weighs 1·5199 grams. A pressure of 17 atmospheres at 10° reduces it to the liquid form, and it may now be purchased in the liquid form secured in small steel bottles like those used for chlorine (p. 96). Cold water dissolves its own volume of hydrogen sulphide, and the solution is used as a test; it is, however, rather quickly decomposed by the oxygen of the air, and should therefore be kept in a tightly closed bottle. Another mode of testing with hydrogen sulphide is to keep a little apparatus (fig. 71) for generating the gas always at hand. A small bottle or flask, to which a bit of bent tube is fitted by a cork, is supplied with a little iron sulphide and water; when it is required for use, a few drops of sulphuric acid are added, and the gas is at once evolved. The experiment completed, the liquid is poured from the bottle, replaced by a little clean water, and the apparatus is again ready for use.

Fig. 71.



Hydrogen sulphide is such an important agent in the chemical laboratory, that it is customary to keep in readiness some form of apparatus for general use by which it may be immediately produced in any desired quantity. Many devices have been proposed to meet this object. One of the most serviceable forms of apparatus is represented in the accompanying figure.

Fig. 72.



It consists of three vessels connected together by flexible tubing. The first, *a*, contains diluted sulphuric acid; the second, *b*, contains sulphide of iron broken into small lumps which are supported upon a layer of broken glass; the third, *c*, is employed as a washing bottle, and is provided with a tap upon the exit tube. When the gas is wanted the bottle of acid is lifted up so that its bottom is about on a level with the shoulder of the second vessel which contains the

sulphide. If the tap is now opened, the liquid runs down, and coming into contact with the sulphide, dissolves it with evolution of sulphuretted hydrogen, which by bubbling through the water placed in the washing bottle, is deprived of any traces of sulphuric acid or iron sulphate which it might carry over. The generation of the gas can be completely controlled by the tap, and soon ceases when this is closed, the pressure of the gas as it accumulates drives the acid liquid back into the first bottle.

Potassium heated in hydrogen sulphide burns with great energy, becoming converted into sulphide, while pure hydrogen remains. The gas is best analysed by heating a piece of tin in a measured volume of it confined over mercury in a bent tube. A volume of hydrogen is left equal in volume to the original gas. Taking this fact into account, and comparing the density of the gas with the density of hydrogen and of red-hot sulphur-vapour, it appears that every volume of hydrogen sulphide contains one volume of hydrogen and half of a volume of sulphur-vapour, the whole condensed into one volume, a constitution precisely analogous to that of water-vapour. This corresponds with its composition by weight, determined by other means—namely, 16 parts of sulphur and one part of hydrogen.

Hydrogen sulphide possesses the properties of an acid : its solution in water reddens litmus paper.

The best test for the presence of this compound is paper wetted with solution of lead acetate, which is blackened by the smallest trace of the gas.

There are few reagents of greater value to the chemist than this substance; when brought in contact with many metallic solutions it gives rise to precipitates, which are often exceedingly characteristic in appearance, and it frequently affords the means of separating metals from each other with the greatest precision and certainty. These precipitates are insoluble sulphides, formed by the mutual decomposition of the metallic oxides or chlorides and hydrogen sulphide, water or hydrochloric acid being produced at the same time. Only those metals are precipitated whose sulphides are insoluble in water and in dilute acids.

Experiments.—With the aid of one of the forms of apparatus already described, cause sulphuretted hydrogen to bubble slowly through the following solutions, carefully observing the result in each case. The solutions should be moderately dilute :—

1. Solution of arsenious oxide acidified with hydrochloric acid. A bright yellow precipitate, As_2S_3, results.

2. Solution of copper sulphate acidified. A dark brown precipitate, CuS, is formed.

3. Solution of zinc sulphate acidified. No visible change is produced.

4. Solution of zinc sulphate mixed with ammonia in excess. A white precipitate, ZnS, is thrown down.

5. Solution of magnesium sulphate, whether alone or mixed

with an acid or with ammonia, gives no precipitate with hydrogen sulphide.

Hydrogen Persulphide.—This very unstable substance is prepared by the following means :—

Equal weights of slaked lime and flowers of sulphur are boiled with 5 or 6 parts of water for half an hour, whereby a deep orange-coloured solution is produced, containing, among other things, calcium bisulphide. This is filtered, and slowly added to an excess of dilute sulphuric acid, with constant agitation. A white precipitate of separated sulphur and calcium sulphate then makes its appearance, together with a quantity of yellow oily-looking matter, which collects at the bottom of the vessel : this is hydrogen persulphide.

This compound is generally regarded as a bisulphide of hydrogen, H_2S_2, analogous to the dioxide, but its great instability prevents the determination of its composition by direct analysis. By treating an alcoholic solution of strychnine with sulphuretted hydrogen, in the presence of air or oxygen, a compound is obtained containing $2C_{21}H_{22}N_2O_2,3H_2S_2$.

Hydrogen persulphide dissolves phosphorus and iodine, forming a phosphorus sulphide and hydrogen iodide respectively, with evolution of sulphuretted hydrogen. With chlorine it forms hydrochloric acid and sulphur chloride, S_2Cl_2. Bromine acts in a similar manner.

Compounds of Sulphur and Halogens.

Sulphur and Chlorine.—Three chlorides of sulphur are known, represented by the formulæ S_2Cl_2, SCl_2, and SCl_4.

The *protochloride*, SCl or S_2Cl_2, is prepared by passing dry chlorine gas into a retort in which sulphur is sublimed at a gentle heat. It then distils over, and may be collected in a receiver surrounded by cold water, and freed from excess of sulphur by redistillation. It is also produced by distilling a mixture of 1 part sulphur with 9 parts of stannic chloride, or 8·5 parts of mercuric chloride.

Sulphur protochloride is a mobile reddish-yellow liquid, having a peculiar, penetrating, disagreeable odour, and fuming strongly in the air. Density 1·687. It boils at 136°. It dissolves in carbon bisulphide, alcohol, and ether, not, however, without decomposition in the two latter. It dissolves sulphur in large quantities, especially when heated. When saturated with sulphur at ordinary temperatures, it forms a clear yellow liquid of density 1·7, and containing altogether 66·7 per cent. sulphur. The solution of sulphur chloride with the excess of sulphur in crude benzol, is used for vulcanising or sulphurising caoutchouc. It is instantly decomposed by water, with formation of hydrochloric and thiosulphuric acids, and separation of sulphur, the thiosulphuric acid in its turn decomposing into sulphur and sulphurous acid : $2S_2Cl_2 + 3H_2O = 4HCl + S_2 + H_2S_2O_3$ (or $H_2SO_3 + S$).

The *dichloride*, SCl_2 or S_2Cl_4, is produced by passing chlorine to saturation into the preceding compound cooled by a mixture of ice and salt, and expelling the excess of chlorine by a stream of carbon dioxide. The product is a deep red liquid which dissociates rapidly by elevation of temperature. When boiled, chlorine is evolved, and ultimately the lower chloride is left as the residue. This compound is decomposed by water like the protochloride.

The *tetrachloride*, SCl_4, is prepared by saturating sulphur protochloride with chlorine at $-20°$. The product contains 81·59 per cent. chlorine and 18·41 sulphur, the numbers calculated from the formula SCl_4 being 81·61 and 18·39. It dissociates rapidly on raising the temperature and seems to be capable of existing only below $-20°$. It is more stable in union with other chlorides. Sulphur tetrachloride is acted upon by sulphuric oxide, producing sulphurous oxy-chloride together with chlorine and sulphurous oxide: thus—

$$SCl_4 + SO_3 = SOCl_2 + Cl_2 + SO_2 .$$

Sulphur and Bromine.—Bromine dissolves sulphur, forming a brown-red liquid probably containing sulphur bromides analogous to sulphur monochloride; but it has not been obtained pure.

Sulphur and Iodine.—These elements combine when heated together, but the product is always a mixture. The compound, S_2I_2, is a blackish-grey crystalline mass. It decomposes at higher temperatures, gives off iodine on exposure to the air, and is insoluble in water. A *hexiodide*, SI_6, is said to be deposited in crystals having the same crystalline form as iodine when a solution of iodine and sulphur in carbon disulphide is left to evaporate. By heating 254 parts of iodine with 32 parts of sulphur, a compound is obtained which smells like iodine, and is used as an external remedy in skin diseases. A cinnabar-red sulphur iodide is also obtained by precipitating iodine trichloride with hydrogen sulphide.

OXIDES AND OXY-ACIDS OF SULPHUR.

Sulphur and Oxygen.—In addition to two imperfectly known oxides, having the formulæ S_2O_3 and S_2O_7, there are two chief compounds of sulphur and oxygen, the names and composition of which are as follows:—

	Composition by Weight.		
	Sulphur.		Oxygen.
Sulphur dioxide or Sulphurous anhydride, SO_2	32	+	32
Sulphur trioxide or Sulphuric anhydride, SO_3	32	+	48

Both these oxides unite with water and with metallic oxides, or the elements thereof, producing salts; those derived from sulphurous anhydride are called sulphites, and those derived from sulphuric

anhydride sulphates. The composition of the hydrogen salts or acids is as follows :—

Sulphurous acid, $H_2SO_3 = H_2O,SO_2$
Sulphuric acid, $H_2SO_4 = H_2O,SO_3$.

The replacement of half or the whole of the hydrogen by metals gives rises to metallic sulphites and sulphates.

By the combination of sulphuric oxide with sulphuric acid in the proportion of SO_3 to H_2SO_4 (or 80 parts by weight of the oxide to 98 of the acid), an acid is formed called disulphuric or pyrosulphuric acid, having the composition $H_2S_2O_7$.

There are also several acids of sulphur, with their corresponding metallic salts, to which there are no corresponding anhydrous oxides, viz.:—

1. *Hyposulphurous Acid*, H_2SO_2, having the composition of sulphurous acid *minus* one atom of oxgyen.

2. *Thiosulphuric Acid*, $H_2S_2O_3$, having the composition of sulphuric acid in which one-fourth of the oxygen is replaced by sulphur.

Closely allied to this acid is—

3. *Seleniosulphuric Acid*, H_2SSeO_3, having the composition of sulphuric acid in which one-fourth of the oxygen is replaced by selenion.

4. A series of acids called *Polythionic Acids*,* in which the same quantities of oxygen and hydrogen are united with quantities of sulphur in the proportion of the numbers 2, 3, 4, 5, viz. :—

Dithionic or Hyposulphuric acid, .	$H_2S_2O_6$
Trithionic acid, ...	$H_2S_3O_6$
Tetrathionic acid, ...	$H_2S_4O_6$
Pentathionic acid, ...	$H_2S_5O_6$.

5. An acid called persulphuric acid, $H_2S_2O_8$, scarcely known except in the form of its metal derivatives or salts.

Sulphur Dioxide, Sulphurous Oxide, or **Anhydride,** SO_2.— This is the product of the combustion of sulphur in dry air, or oxygen gas. It is most conveniently prepared by heating undiluted sulphuric acid with copper clippings, whereby cupric sulphate, water, and sulphur dioxide are formed, the last being given off as gas :—

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

A small quantity of copper sulphide is formed at the same time, and this accounts for the black colour of the residue. The experiment may be performed in the same apparatus as that used in the production of chlorine and hydrochloric acid, and the gas may be collected by displacement of air in the same way.

Another very simple and cheap method of preparing sulphur dioxide consists in heating concentrated sulphuric acid with charcoal ;

* From πολύς, many, and θεῖον, sulphur.

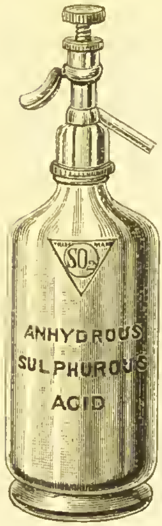
a very regular evolution of sulphurous oxide, mixed with half its volume of carbon dioxide, is thus obtained—

$$2H_2SO_4 + C = 2SO_2 + CO_2 + 2H_2O.$$

This process may be employed in the manufacture of sulphites, as the carbon dioxide will not be retained by an alkali so long as the sulphur dioxide is in excess.

Sulphur dioxide is a colourless gas, having the peculiar suffocating odour of burning brimstone; it instantly extinguishes flame, and is quite irrespirable. Its density is 2·21; a litre weighs 2·8605 grams; 100 cubic inches weigh 68·69 grains. At about $-10°$ C. under the ordinary pressure of the atmosphere, this gas condenses to a colourless, limpid liquid, very expansible by heat. In this form it is now manufactured and may be obtained stored in glass bottles such as shown in figure 73, from which a supply of the gas may be obtained by releasing the screw tap. Cold water dissolves more than thirty times its volume of sulphur dioxide. The solution, which contains hydrogen sulphite or sulphurous acid, H_2SO_3, may be kept unchanged so long as air is excluded, but access of oxygen gradually converts the sulphurous into sulphuric acid, although dry sulphur dioxide and oxygen gases may remain in contact for any length of time without change. When sulphur dioxide and aqueous vapour are passed into a vessel cooled to about 21° F. ($-6°$ C.), a crystalline hydrate forms, which contains about 24·2 sulphur dioxide to 75·8 water, or $H_2SO_3.10H_2O$.

Fig. 73.



Sulphur dioxide gas contains its own volume of oxygen, and therefore corresponds in composition to carbon dioxide. Sulphurous acid, H_2SO_3, is not known except in solution and in the hydrate already mentioned; but it forms two well-defined classes of salts represented respectively by the formulæ $MHSO_3$ and M_2SO_3, where M stands for such a metal as sodium or potassium.

Sulphurous acid has bleaching properties; it is used in the arts for bleaching woollen goods and straw-plait, which are injured by chlorine. A piece of blue litmus paper plunged into the moist gas is first reddened and then slowly bleached.

The sulphites of the alkalis are soluble and crystallisable, and in general resemble carbonates; they are easily formed by direct combination. The sulphites of barium, strontium, and calcium are insoluble in water, but soluble in hydrochloric acid. The stronger acids decompose them; nitric acid converts them by oxidising into sulphates. The soluble sulphites act as powerful reducing agents, and are much used in that capacity in chemical analysis.

Sulphur dioxide unites, under the influence of sunlight, with chlorine, forming the compound, SO_2Cl_2, which will be described later.

Experiments.—1. Prepare a flask as described under "Chlorine" (p. 95). Place in it about an ounce of thin copper wire or clippings, and add through the funnel about twice that weight of strong sulphuric acid. Heat gently; the evolution of gas begins at about 150°. After time has been allowed for the expulsion of the air from the flask, let the gas pass by means of the delivery-tube to the bottom of a small dry cylinder, the mouth of which is covered by a card. The cylinder may be known to be full when a lighted taper dipped into it is put out. Fill several jars or cylinders in this manner.

2. Cover one of them by a glass plate, and place it mouth downwards in a dish of water. The gas quickly dissolves, and the water ascends into the cylinder, filling it completely, unless the gas contained air.

3. Dip into the solution thus formed, or into the moist gas, a piece of blue litmus paper; it becomes red.

4. Suspend in the gas a bunch of violets or other purple-coloured flowers; they are bleached.

5. Prepare a small jar full of sulphuretted hydrogen, and, keeping it covered by a glass plate, place it mouth to mouth with a similar jar of sulphur dioxide. Then draw away the plates, so that the gases may mix. Water is formed, and a cloud of solid sulphur is deposited—

$$SO_2 + 2H_2S = 3S + 2H_2O.$$

A similar effect is produced by passing the gases successively, or at the same time, through the same portion of water. A small quantity of pentathionic acid is formed at the same time (see p. 138).

Sulphur Trioxide, Sulphuric Oxide or **Anhydride,** SO_3.—This compound cannot be obtained by the direct union of sulphur dioxide and oxygen at any temperature, but it is readily formed when a mixture of these gases, thoroughly dried, is passed over heated spongy platinum. It may be obtained by distilling the most concentrated sulphuric acid with phosphoric oxide, which then abstracts water and sets the sulphuric oxide free. It may also be prepared from fuming oil of vitriol (see p. 135), which may be regarded as a solution of sulphuric oxide in sulphuric acid. On gently heating this liquid in a retort connected with a receiver cooled by ice, the sulphuric oxide distils over, and condenses into beautiful white silky crystals, resembling asbestos.

Sulphuric oxide is manufactured in considerable quantity by causing a mixture of sulphur dioxide and excess of dry air to pass through glazed earthenware pipes containing fragments of platinised asbestos heated to low redness. The sulphuric oxide is condensed in a series of double-necked bottles.

Sulphuric oxide, when thrown into water, hisses like a red-hot iron, from the violence with which combination occurs: the product is sulphuric acid. When exposed to the air, even for a few moments, it liquefies by absorption of moisture. It unites with ammoniacal gas, forming a salt called *ammonium sulphamate*, the nature of which will be explained further on.

Melted sulphuric oxide undergoes very great expansion by heat, its mean coefficient of expansion between 25° and 45° being 0·0027 for 1° C., that is to say, more than two-thirds as great as that of gases. Liquid sulphuric oxide mixes in all proportions with hydrogen sulphate, H_2SO_4. Some remarkable phenomena exhibited by these solutions will be described further on (p. 135).

Sulphuric Acid or **Hydrogen Sulphate**, H_2SO_4. —The manufacture of this important acid depends upon the fact that, when sulphur dioxide, nitrogen peroxide, and water are present together in certain proportions, the sulphur dioxide becomes oxidised at the expense of the nitrogen peroxide, which, by the loss of one-half of its oxygen, is reduced to nitric oxide. Inasmuch as nitric oxide has the power of uniting with oxygen in the free gaseous state, reproducing nitric peroxide, it is obvious that a small quantity of nitric oxide may serve to cause the oxidation of an indefinitely large quantity of sulphur dioxide into sulphuric acid. It is only necessary to supply sulphur dioxide, air, and water continuously into a chamber in which the oxide of nitrogen is already present.

The material from which the requisite sulphur is obtained, is generally iron pyrites, a mineral which is imported in large quantities, chiefly from Spain. This is roasted in a series of ovens or kilns (fig. 74, *a*), in a current of air which is admitted in considerable excess. The sulphur burns off, leaving a residue which consists of oxide of iron, together with small quantities of oxide of copper and silver. This forms the material for a distinct series of operations by which these metals are separated. The gases from the pyrites burners, consisting of a mixture of sulphur dioxide and atmospheric oxygen and nitrogen, pass together through a wide flue, at the extremity of which are placed pots (*b*) containing a little nitrate of sodium mixed with oil of vitriol. The object of this is to supply the mixture of nitric acid and nitrogen oxides which, as already mentioned, play an important part in bringing about the oxidation of the sulphurous oxide. All these gases and vapours are conducted into the first of a series of mixing chambers (*c*) built of sheet lead, supported by timber framing. These chambers are generally of very large dimensions, having very often a capacity of 100,000 cubic feet or more. Here jets of steam from a boiler below (*d*) are introduced at intervals, and supply the water necessary for the formation of sulphuric acid.

The principal reactions which go on may be broadly represented in the two following equations, of which the first represents the oxidation of the elements of sulphurous acid into sulphuric acid by the nitric peroxide :—

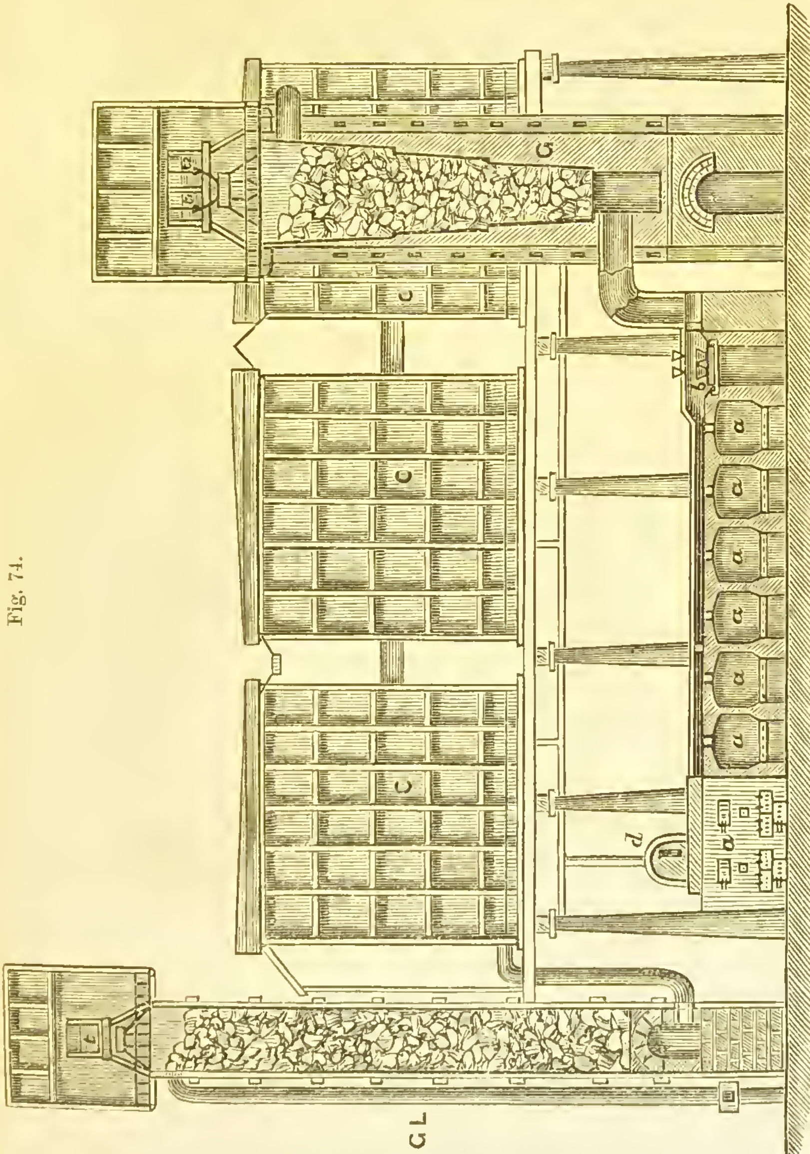
$$NO_2 + SO_2 + H_2O = NO + H_2SO_4.$$

The second expresses the restoration of the oxygen to the nitric oxide by the air which is always present :—

$$NO + O = NO_2.$$

It will thus be perceived that a relatively small quantity of nitric oxide in the presence of a continuous supply of sulphurous oxide,

Fig. 74.

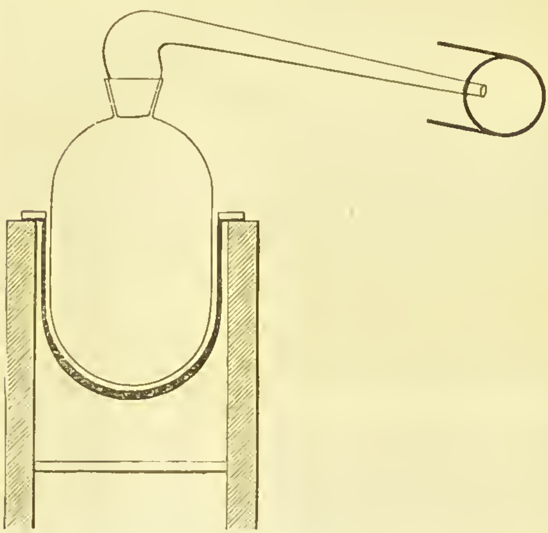


air, and steam, is capable of converting this mixture into sulphuric acid.

The acid thus produced collects in the liquid form at the bottom of the chambers, and when it has attained a certain degree of concentration (about 60 to 65 per cent. of H_2SO_4), the liquid is drawn off and concentrated, at first by evaporation in open leaden pans, subsequently in boilers of glass or of platinum, in which weak acid distils over and is saved, whilst the concentrated acid remains behind. The latter when cold has a density of 1·84, or thereabouts : it is then transferred to "carboys" or large glass bottles fitted in baskets for sale.

Fig. 75 represents one of the glass vessels used for concentrating sulphuric acid. Each of these retorts, which are usually capable of holding some twenty gallons of the acid, is set in a separate iron pot placed over a fire and the neck of the retort passes into a horizontal leaden pipe which serves as a receiver common to a series of twelve or more. As the acid boils, water, accompanied by a little acid passes over, the carbonaceous impurities usually present in the residual acid are at the same time oxidised, and after a time the residual liquid becomes perfectly colourless.

Fig. 75.



At the end of the series of reactions which proceed in the vitriol chambers, after the condensation of the sulphuric acid, the nitrogen of the air and the greater part of the nitric oxide remain in the gaseous form. It was formerly the custom to allow these gases to escape into the atmosphere. Now it is not only to the interest of the manufacturer to avoid loss of the nitric oxide, but the Alkali Works Regulation Act forbids the discharge of gases of this kind into the atmosphere in quantity exceeding a certain amount (equivalent altogether to 4 grains of SO_3 per cubic foot). It is therefore the practice in all well conducted works to add to the apparatus already described an arrangement for collecting the nitrous gases from the last of the leaden chambers, and another for restoring them to the first of the series. The former consists of a tower (GL) filled with coke, upon which a stream of concentrated sulphuric acid continually flows from a tank (t) placed at the top. Meeting the gases issuing from the chambers, it absorbs from them the oxides of nitro-

gen, forming nitrosyl sulphate, which remains dissolved in excess of sulphuric acid—

$$2NO + O + 2H_2SO_4 = 2NOHSO_4 + H_2O.$$

In order to recover the nitric oxide from this compound the acid solution may be decomposed by steam, or more generally it is forced up to a tank (t^1) placed at the top of another tower (G), filled with flint stones and placed in communication at the upper part with the first chamber of the series, and, at the bottom, connected with the flue leading from the pyrites burners. A second tank (t^2), at the top of the same tower, is filled with the, comparatively, weak acid from the chambers. The two liquids are allowed to flow in regulated streams, so as to mix in the upper part of the column of stones. The reaction which occurs is produced by the water of the weaker acid decomposing the nitrous constituent of the stronger, thus

$$2NOHSO_4 + H_2O = 2H_2SO_4 + NO_2 + NO.$$

The gases thus liberated are swept back by the ascending current of hot sulphurous gas and air and pass into the leaden chamber, while the sulphuric acid, deprived of nitrogen compounds, runs out at the bottom into the leaden evaporating pan where the process of concentration goes forward. The former of these for absorption, is usually called the Gay-Lussac tower, and the denitrating column having been introduced by Mr Glover a few years ago, is generally known by his name.

Experiment.—When sulphur dioxide and nitrogen tetroxide are passed by separate tubes into a large glass globe, symptoms of chemical action become immediately evident, and after a little time a white crystalline matter is observed to condense on the sides of the vessel. This substance consists of the nitrosyl sulphate mentioned above, combined with various proportions of sulphuric acid. If now a little water is added to the contents of the flask, the crystals dissolve with effervescence, and the gases present are again reddened by the production of nitric peroxide.

It was formerly supposed that the production of this compound was indispensable to the success of the process of sulphuric acid making. Crystals are, however, never found in the leaden chambers; their production would indicate considerable deficiency of steam.

Sulphuric acid made by burning iron pyrites, or poor copper ore, or zinc-blende, instead of Sicilian sulphur, very frequently contains arsenic, from which it may be freed, however, by heating it with a small quantity of sodium chloride, or by passing through the heated acid a current of hydrochloric acid gas, whereby the arsenic is volatilised as trichloride.

The most concentrated sulphuric acid, or *oil of vitriol*, as it is often called, is a definite combination of 40 parts sulphuric oxide and 9 parts of water, and is represented by the formula H_2O,SO_3 or H_2SO_4. It is a colourless oily liquid, having a density of about

1·842, of intensely acid characters. Organic matter is rapidly charred and destroyed by it. At the temperature of −26° C. (−15° F.) it freezes; at 327° C. (620° F.) it boils, and may be distilled. Oil of vitriol has a most energetic attraction for water; it withdraws aqueous vapour from the air, and when it is diluted with water, great heat is evolved, so that the mixture always requires to be made with caution. Oil of vitriol is not the only hydrate of sulphuric oxide; three others are known to exist. When the fuming oil of vitriol of Nordhausen is exposed to a low temperature, a white crystalline substance separates, which is a hydrate containing half as much water as the common liquid acid, *i.e.*, $H_2O,2SO_3$ or $H_2S_2O_7$. Further, a mixture of 98 parts of strong liquid acid and 18 parts of water, $2H_2O,SO_3$ or H_2SO_4,H_2O, congeals or crystallises at a temperature above 0° C., and remains solid even at 7·2° C. (45° F.). This is usually known as *glacial* sulphuric acid. Lastly, when a very dilute acid is concentrated by evaporation in a vacuum over a surface of oil of vitriol, the evaporation stops when the sulphuric oxide and water bear to each other the proportion of 80 to 54, answering to the formula $3H_2O,SO_3$ or $H_2SO_4,2H_2O$.

Sulphuric acid acts readily on metallic oxides, converting them into sulphates. It also decomposes all carbonates at the common temperature, expelling carbon dioxide with effervescence. With the aid of heat it likewise decomposes all other salts, such as chlorides and nitrates, which yield acids more volatile than itself. The sulphates are a very important class of salts, many of them being extensively used in the arts. Most sulphates are soluble in water, but they are all insoluble in alcohol. The barium, strontium, calcium, and lead salts are insoluble, or very slightly soluble, in water, and are formed by precipitating a soluble salt of either of those metals with sulphuric acid or a soluble metallic sulphate.

Experiments.—1. Place in a small beaker a few ounces of water, then inclining it slightly, pour in about one-fourth as much strong sulphuric acid, so that it runs down the side to the bottom of the water. Note that sulphuric acid is nearly twice as dense as water. Then with a glass rod stir the two liquids together. Note that much heat is developed. It should be remembered, with a view to safety, that water should never be added to strong sulphuric acid, and the acid should in no case be added to hot water. In either case a violent ebullition, almost amounting to explosion, may ensue, and the scalding liquid may be thrown out of the vessel.

2. Add more water to the preceding mixture, so as to dilute it considerably. Then with the aid of a brush, trace some characters with this liquid upon a sheet of paper, and dry the latter in an oven or before the fire. The acid will blacken the paper. A similar effect is produced by concentrated sulphuric acid upon wood, sugar, and other organic substances.

3. Powder a few crystals of blue vitriol or copper sulphate, $CuSO_45H_2O$, and shake in a test-tube with sufficient strong sulphuric

acid to make a fluid mixture. In a short time the powder becomes white in consequence of the abstraction of the crystalline water by the acid.

4. Place about half an ounce (10 or 15 grams) of strong sulphuric acid in a small beaker, weigh the whole, and then leave the acid exposed to the air for a few hours. Weigh again, and note the considerable increase of weight due to absorption of water from the air.

5. Pour strong sulphuric acid into two dry test-tubes till it occupies about half an inch at the bottom. Into each drop a piece of granulated zinc, and observe that no appreciable action occurs. Now dilute the one portion of acid with several times its bulk of water; hydrogen is evolved. Heat the other; sulphur dioxide is evolved.

6. To some diluted sulphuric acid add a solution of barium chloride: a white precipitate of barium sulphate is formed, which does not dissolve in hydrochloric or nitric acid. Apply the same test to sodium sulphate, copper sulphate, alum, and other sulphates.

Disulphuric, or Pyrosulphuric Acid, $H_2S_2O_7$ (also called *Fuming Sulphuric Acid* and *Nordhausen Sulphuric Acid*).—This acid contains the elements of one molecule of sulphuric oxide and one molecule of sulphuric acid, or of two molecules of sulphuric acid *minus* one molecule of water:

$$H_2S_2O_7 = SO_3,H_2SO_4 = 2H_2SO_4 - H_2O.$$

It may be obtained of definite composition and in the crystalline form by adding sulphuric oxide to strong sulphuric acid, in the proportion above indicated. The resulting crystals melt at 35°. It is also prepared from the impure ferric sulphate obtained by exposing ordinary ferrous sulphate (green vitriol) to a moderate heat in contact with the air. This ferric sulphate is distilled in earthen retorts arranged in a reverberatory furnace, and the distillate, consisting chiefly of sulphuric oxide, is received in a small quantity of water, or more frequently in ordinary strong sulphuric acid. A brown fuming liquid is thus obtained, which has a density of 1·9, solidifies at 0° in colourless crystals, and is resolved at a gentle heat into SO_3 which distils over, and H_2SO_4 which remains behind.

The manufacture of fuming sulphuric acid in the manner just described was first practised at Nordhausen in Saxony, and appears to have been known since the fifteenth century; but it is now carried on almost exclusively in Bohemia. An easier and more productive method of obtaining the sulphuric oxide required for its formation is that already described (p. 127). Fuming sulphuric acid was until lately employed only for dissolving indigo, but it is now used in very large quantities for dissolving anthraquinone for the manufacture of artificial alizarin, a red dye much used in calico printing.

For this purpose solutions of sulphuric anhydride in sulphuric acid are prepared of various strengths. These mixtures present

some curious anomalies in regard to their melting point. Thus, if the proportion of SO_3 added is 30 per cent. or less, the product is liquid ; the addition of 40 to 46 per cent. gives rise to a crystalline mass, probably consisting chiefly of the compound $H_2SO_4.SO_3$, which contains nearly 45 per cent. of SO_3. If now a further quantity of the anhydride is added, so as to amount to 60 to 69 per cent., a liquid is obtained, whilst a further addition, amounting to 72 to 82 per cent. of SO_3, gives rise again to a crystalline product.

The pyrosulphates, that of potassium, for example, which has the composition $K_2S_2O_7$, or K_2SO_4,SO_3, are prepared by heating the normal sulphates with excess of sulphuric acid to low redness. When strongly heated, they give off sulphuric oxide, and are converted into sulphates.

Hyposulphurous Acid, H_2SO_2 (also called *Hydrosulphurous Acid*).—This acid is formed by the action of zinc on an aqueous solution of sulphurous acid. The zinc dissolves without evolution of hydrogen, merely removing an atom of oxygen. A yellow solution is thereby formed, which possesses much greater decolorising power than sulphurous acid itself, and quickly reduces the metals from salts of silver and mercury. This solution is, however, very unstable, and quickly loses its bleaching power. A more definite product is obtained by immersing clippings of zinc in a concentrated solution of acid sodium sulphite, $NaHSO_3$, contained in a closed vessel, whereby sodium hyposulphite, $NaHSO_2$, and zinc-sodium sulphite, $Na_2Zn(SO_3)_2$, are produced, the latter crystallising out. To isolate the hyposulphite, the liquid is decanted, after about half an hour, into a flask three-fourths filled with strong alcohol, and the mouth of the flask is closed. A crystalline precipitate immediately forms, consisting for the most part of zinc-sodium sulphite, while nearly all the hyposulphite remains dissolved in the alcohol. The solution, decanted into a flask quite filled with it, well closed, and left in a cool place, solidifies in a few hours to a mass of slender colourless needles, consisting of s o d i u m h y p o s u l p h i t e, which must be quickly pressed between folds of linen, and dried in a vacuum, as it becomes very hot if exposed to the air in the moist state ; when dry, however, it is not affected by oxygen. This salt is very soluble in water, soluble also in dilute alcohol, the solutions exhibiting all the bleaching and reducing properties above described. The crystals when exposed to the air are completely converted into acid sodium sulphite, $NaHSO_3$. By heating them with oxalic acid, hyposulphurous acid is obtained, as a deep orange-coloured strongly bleaching liquid, which quickly decomposes, becoming colourless, and depositing sulphur.

Thiosulphuric Acid, $H_2S_2O_3$ (formerly called *Hyposulphurous Acid*).—By digesting sulphur with a solution of potassium or sodium sulphite, a portion of that substance is dissolved, and the liquid, by slow evaporation, yields crystals of thiosulphate.

The important salt commonly known as sodium hyposulphite or briefly 'hypo' is, however, more commonly manufactured by exposing alkali-maker's waste to the air till partly oxidised, then extracting with water and precipitating with carbonate of sodium. After filtering off the calcium carbonate thrown down, the liquid is evaporated to a small bulk, and crystals consisting of $Na_2S_2O_3,5H_2O$ are then deposited.

Thiosulphuric acid is scarcely known, for it cannot be isolated; when hydrochloric acid is added to a solution of a thiosulphate, the acid of the latter is almost instantly resolved into sulphur, which precipitates, and sulphurous acid, easily recognised by its odour. In a very dilute solution, however, it appears to remain undecomposed for some time. The alkaline thiosulphates readily dissolve certain salts of silver, as the chloride, which are insoluble in water—a property which has conferred upon them a considerable importance in relation to the art of photography. They are also much used as 'antichlore' for removing the last traces of chlorine from bleached goods.

Thiosulphates of the heavy metals, such as silver, copper, and lead, are easily resolved in the presence of water into metallic sulphide and sulphuric acid. For example:

$$Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4 .$$

Seleniosulphuric or **Thioselenic Acid,** H_2SeSO_3.—The salts of this acid, having the composition of sulphuric acid in which 1 atom of oxygen is replaced by selenion, are formed by direct addition of selenion to sulphites. When selenion is digested with a solution of neutral potassium sulphite, and the easily decomposible liquid, after being filtered from the selenion which separates on cooling and dilution with water, is left to evaporate at ordinary temperatures, there crystallises out, first a sparingly soluble seleniferous salt in small shining prisms, afterwards a much more soluble salt, which is the chief product of the reaction, while the excess of sulphite remains in the mother-liquor.

Potassium seleniosulphate, K_2SeSO_3, crystallises readily, even from small quantities of solution, in large, very thin, six-sided tables belonging to the rhombic system, which deliquesce in moist air, and effloresce with partial loss of water over oil of vitriol. Water precipitates a portion, and acids throw down the whole, of the selenion from the aqueous solution; barium chloride and baryta water precipitate barium sulphite and selenion; calcium and manganese salts give rise to a similar decomposition. With ammoniacal silver solution the seleniosulphate forms a precipitate of silver selenide together with potassium sulphate:

$$K_2SeSO_3 + Ag_2O = Ag_2Se + K_2SO_4 .$$

Dithionic, or **Hyposulphuric Acid,** $H_2S_2O_6$.—This acid is prepared by suspending finely divided manganese dioxide in water arti-

ficially cooled, and passing a stream of sulphur dioxide through the liquid; $MnO_2+2SO_2=MnS_2O_6$. The manganese dithionate thus prepared is decomposed by a solution of pure barium hydrate; and the barium salt, in turn, by enough sulphuric acid to precipitate the barium. The solution of dithionic acid may be concentrated by evaporation in a vacuum, until it acquires a density of 1·347; on further concentration, it decomposes into sulphuric and sulphurous acids. It has no odour, is very sour, and forms soluble salts with baryta, lime, and lead oxide.

Trithionic Acid, $H_2S_3O_6$.—A salt of this acid is formed by gently heating with sulphur a solution of potassium acid sulphite: $2KHSO_3 + 2S = K_2S_3O_6 + H_2S$. It is also produced by the action of sulphur dioxide on potassium thiosulphate: $2K_2S_2O_3 + 3SO_2 = 2K_2S_3O_6 + S$. Its salts bear a great resemblance to those of thiosulphuric acid, but differ completely in composition, while the acid itself is not quite so prone to change. It is obtained by decomposing the potassium salt with hydrofluosilicic acid: it may be concentrated under the receiver of the air pump, but is gradually decomposed into sulphurous and sulphuric acids, and free sulphur.

Tetrathionic Acid, $H_2S_4O_6$.—When iodine is added to a solution of a thiosulphate, a clear colourless solution is obtained, which, besides iodide, contains a tetrathionate for example: $2BaS_2O_3 + I_2 = BaI_2 + BaS_4O_6$. By suitable means, the acid can be eliminated, and obtained in a state of solution. It very closely resembles dithionic acid.

Pentathionic Acid, $H_2S_5O_6$.—This acid was discovered by Wackenroder, who formed it by the action of hydrogen sulphide on sulphurous acid: $5H_2SO_3 + 5H_2S = H_2S_5O_6 + 9H_2O + S_5$. This liquid, however, contains the other polythionic acids which are all decomposed by hydrogen sulphide, so that if the action of the latter is continued, sulphur and water are the only final products. Pentathionic acid is colourless and inodorous, of acid and bitter taste, and capable of being concentrated to a considerable extent by cautious evaporation.

Under the influence of heat, it is decomposed into sulphur, sulphurous and sulphuric acids, and hydrogen sulphide. The salts of pentathionic acid are nearly all soluble. The potassium salt crystallises in prisms consisting of $2K_2S_5O_6 \cdot 3H_2O$; the copper salt forms small, fine blue crystals, containing $CuS_5O_6 \cdot 4H_2O$.

An ammoniacal solution of silver nitrate causes in a solution of soluble pentathionate a brown coloration, and by degrees a black precipitate is thrown down from the mixture. This reaction is not produced in a solution of tri- or tetrathionate, thiosulphate or sulphite (Debus). Alkalis added to a solution of a pentathionate cause an immediate precipitate of sulphur, but potassium pentathionate may be recrystallised without change from solutions acidified with sul-

phuric or acetic acid. Pentathionate is also formed by the regulated action of hydrogen sulphide upon soluble dithionates and tetrathionates.

Oxychlorides. — 1. *Sulphurous oxychloride or Thionyl chloride*, $SOCl_2$.—This compound is derived from sulphurous acid, SO_3H_2 or $SO(HO)_2$, by the substitution of 2Cl for 2HO. It is formed by the action of water, alcohols, acids, etc., on the chlorides of sulphur; but is more easily prepared by the action of phosphorus pentachloride on sulphurous oxide, or by that of phosphorus oxychloride on calcium sulphite:

$$SO_2 + PCl_5 = POCl_3 + SOCl_2.$$
$$3CaSO_3 + 2POCl_3 = Ca_3P_2O_8 + 3SOCl_2.$$

It is separated by distillation from the fixed calcium phosphate produced simultaneously in the second, and by fractional distillation from the phosphorus oxychloride produced in the first reaction.

Sulphurous chloride is a colourless, strongly refracting liquid, which boils at 82°. It is decomposed by water, yielding hydrochloric and sulphurous acids; and by alcohols with formation of alcoholic chlorides and sulphurous acid, thus:

$$SOCl_2 + 2H_2O = 2HCl + H_2SO_3$$
$$SOCl_2 + \underset{\text{Ethyl alcohol.}}{2(C_2H_5)HO} = \underset{\text{Ethyl chloride.}}{2C_2H_5Cl} + H_2SO_3.$$

Sulphuric oxychloride, or *Sulphuryl chloride*, SO_2Cl_2, is formed by prolonged exposure of a mixture of chlorine and sulphurous oxide gases to strong sunshine, or by bringing these two gases together in the presence of some solvent of both, such as melted camphor or glacial acetic acid; but it is best prepared by heating the next compound in a sealed tube for some hours to 200°, and distilling the resulting liquid, collecting the portions which come over at about 70°.

Sulphuric oxychloride is a colourless fuming liquid, of density 1·66. It boils at 70°, and may be distilled unchanged over caustic lime or baryta. When poured into water, it sinks in the form of oily drops, which gradually disappear, being converted into hydrochloric and sulphuric acids:

$$SO_2Cl_2 + 2H_2O = 2HCl + H_2SO_4.$$

With alcohol it behaves in a similar manner, thus:

$$SO_2Cl_2 + 2(C_2H_5)HO = 2C_2H_5Cl + H_2SO_4.$$

In the actual reaction, however, the sulphuric acid is converted into ethylsulphuric acid by the intervention of another molecule of alcohol:

$$H_2SO_4 + (C_2H_5)HO = H_2O + (C_2H_5)HSO_4.$$

Sulphuric Hydroxichloride or *Sulphuric Chlorhydrin*, $HClSO_3$, or $SO_2(HO)Cl$ (also called *Chlorosulphonic Acid*).—This compound is intermediate in composition between sulphuric acid and sulphuric oxychloride, and is derived from sulphuric acid, SO_4H_2 or $SO_2(HO)_2$, by

the substitution of Cl for HO. It is the chief product of the action of phosphorus pentachloride on strong sulphuric acid :

$$SO_2(HO)(HO) + PCl_5 = POCl_3 + HCl + SO_2(HO)Cl.$$

It may also be obtained pure by treating sulphuric acid with phosphorus oxychloride, hydrochloric and metaphosphoric acid being produced at the same time :

$$2SO_2(HO)(HO) + POCl_3 = 2SO_2(HO)Cl + HCl + HPO_3.$$

It is also formed by the action of a limited quantity of water on sulphuric oxychloride :

$$SO_2Cl_2 + H_2O = HCl + HClSO_3,$$

and by direct combination of sulphur trioxide and hydrochloric acid.

Sulphuric hydroxychloride is a colourless liquid, which boils at about 150°, being at the same time partially resolved into sulphuric acid and sulphuric chloride : $2HClSO_3 = H_2SO_4 + Cl_2SO_2$. It is violently decomposed by water, with formation of hydrochloric and sulphuric acids. It forms definite salts in which its hydrogen is replaced by metals. Thus it dissolves sodium chloride at a gentle heat, with evolution of hydrochloric acid, and formation of the salt $NaClSO_3$.

Pyrosulphuric oxychloride, $S_2O_5Cl_2$ or $(SO_2Cl)_2O$. This compound is formed on heating together phosphorus pentachloride and sulphur trioxide :

$$PCl_5 + 2SO_3 = S_2O_5Cl_2 + POCl_3,$$

and by the action of phosphorus pentachloride on sulphuric hydroxychloride :

$$PCl_5 + 2SO_2ClOH = (SO_2Cl)_2O + POCl_3 + 2HCl.$$

It is a colourless oily liquid of density 1·819 at 18°, boiling at 146°. In contact with water it decomposes slowly and noiselessly, and is thus distinguished from sulphuric hydroxychloride, which is rapidly decomposed, with almost explosive violence, when thrown into water.

Persulphuric Acid and Persulphates, $M'_2S_2O_8$.—When a solution of acid potassium sulphate is subjected to electrolysis, the salt undergoes oxidation at the positive pole, thus :

$$2HKSO_4 + O = H_2O + K_2S_2O_8.$$

Potassium persulphate is sparingly soluble and crystallises in tabular crystals. Other salts have been obtained in a similar manner, the acid itself being formed during the electrolysis of dilute sulphuric acid. The persulphates are all unstable, and upon the application of heat give off oxygen gas : hence they all possess strong oxidising powers, liberating chlorine, bleaching organic colouring matters, and giving precipitates of peroxides when added to solutions of the heavy metals, such as iron, copper, nickel, cobalt.

SELENION.

Symbol, Se. Atomic weight, 79. Vapour-density, 79.

This substance, much resembling sulphur in its chemical relations, occurs frequently, associated in small quantities with that element, or replacing it in certain metallic combinations, as in the lead selenide of Clausthal in the Hartz. To separate it, the pulverised ore is treated with hydrochloric acid to dissolve earthy carbonates, and the washed and dried residue is ignited for some time with an equal quantity of black flux (a mixture of potassium carbonate and charcoal). The selenion is thereby converted into potassium selenide, which by treatment with boiling water is dissolved away from the oxides formed at the same time. The solution when exposed to the air absorbs oxygen, and yields the selenion as a grey deposit, which may be purified by washing, drying, and distillation.

A better method consists in turning to account the reddish deposit formed in the flues, and in the Glover tower when seleniferous pyrites is employed for the manufacture of sulphuric acid. This deposit is oxidised into selenic acid, H_2SeO_4, by boiling with nitric acid. The solution thus obtained is reduced to selenious acid when boiled with strong hydrochloric acid, and from this the selenion can be precipitated by sulphur dioxide:

$$H_2SeO_3 + 2SO_2 + H_2O = Se + 2H_2SO_4 .$$

Selenion, like sulphur, exists in several allotropic modifications, some of which are distinguished by being soluble, others by being insoluble in carbon bisulphide *a. Soluble modifications:* selenion in this form is obtained as a finely divided brick-red powder on passing a current of sulphur dioxide into a cold solution of selenious acid, or as a black crystalline powder when the same gas is passed through a hot solution of the acid. It crystallises from solution in carbon sulphide in small dark red monoclinic crystals, isomorphous with monoclinic sulphur, and having a density of 4·5. It has no definite melting point, but softens gradually when heated.—*β. Insoluble Selenion* is obtained by quickly cooling melted selenion to 210°, and keeping the melted mass at this temperature for some time, whereupon it ultimately solidifies to a granular crystalline mass, the temperature then suddenly rising to 217°. The solid selenion thus obtained has a density of 4·8, and is insoluble in carbon sulphide. It melts constantly at 217°, and is converted by rapid cooling into the amorphous soluble variety. Both modifications dissolve in selenion chloride, the selenion separating therefrom in the insoluble form. Selenion boils somewhat below 700°, forming a dark red vapour, which condenses either in the form of scarlet 'flowers,' or in dark shining drops.

The vapour-density of selenion, like that of sulphur, diminishes very rapidly as its temperature rises, being 110·7 (hydrogen being

taken as unity) at 860°, and 81·5 at 1420°, which does not differ greatly from the theoretical density.

Elemental selenion conducts electricity, and its conducting power is increased by exposure to light, and diminished by heating. Exposure to diffused daylight immediately diminishes the electrical resistance of selenion to one-half of what it was before, but on cutting off the light, the resistance slowly increases, and soon reaches its original amount.

Selenion when heated in the air burns with a pale blue flame, emitting an odour of decayed horse-radish, due to the formation of an oxide.

Hydrogen Selenide, H_2Se.—This compound is formed by the action of dilute sulphuric acid on selenide of potassium or iron. It is very much like hydrogen sulphide, being a colourless gas, freely soluble in water, and decomposing metallic solutions, with formation of insoluble selenides. It acts very powerfully on the mucous membrane of the nose, exciting catarrhal symptoms and temporarily destroying the sense of smell.

Selenion Chlorides.—The *protochloride*, Se_2Cl_2, formed by passing chlorine gas over selenion, is a brown oily liquid, which readily dissolves selenion and deposits it in the insoluble form on cooling. It is slowly decomposed by water, yielding selenious acid, hydrochloric acid, and free selenion: $2Se_2Cl_2 + 3H_2O = H_2SeO_3 + 3Se + 4HCl$.

The *tetrachloride*, $SeCl_4$, is obtained by the further action of chlorine on the protochloride, or by heating the dioxide with phosphorus pentachloride: $3SeO_2 + 3PCl_5 = 3SeCl_4 + P_2O_5 + POCl_3$. It is a white solid body, which, when heated, volatilises without previous fusion, and sublimes in small crystals. It dissolves in water, forming hydrochloric and selenious acids: $SeCl_4 + 3H_2O = 4HCl + H_2SeO_3$.

Selenion Bromides.—The *protobromide*, Se_2Br_2, formed by heating together equal weights of bromine and selenion, is a black semi-opaque liquid, having a density of 3·6 at 15°. It smells like sulphur protochloride, and stains the skin brown red. It is decomposed by heat and by the action of water, yielding in the latter case hydrobromic and selenious acids.—The *tetrabromide*, $SeBr_4$, formed by the further action of bromine on the protobromide, is an orange-red crystalline powder, which volatilises without decomposition between 75° and 80°, and sublimes in black hexagonal scales. It smells like sulphur chloride, decomposes in moist air into bromine and the protobromide, and dissolves in excess of water, with formation of hydrobromic and selenious acids.

Selenion Iodides.—The *proto-iodide*, Se_2I_2, formed by direct combination, is a black shining crystalline body melting at 68–70°,

with slight evolution of iodine. It is resolved into its elements at a higher temperature, and is decomposed by water like the corresponding chloride and bromide.—The *tetra-iodide*, SeI_4, is a dark-coloured granular crystalline mass, melting at 75-80° to a brownish-black liquid, translucent in thin films. At a higher temperature it is resolved into its elements.

Oxides and Oxy-acids of Selenion.—Two oxides of selenion are known. The one containing the smaller proportion of oxygen is formed by the imperfect combustion of selenion in air or oxygen gas. It is a colourless gas, which is the source of the peculiar horse-radish odour above mentioned. Its composition is not known.

The higher oxide, selenious oxide or selenion dioxide, SeO_2, is produced by burning selenion in a stream of oxygen gas. It is a white solid substance, which absorbs water rapidly, forming selenious acid.

Selenious acid, H_2SeO_3 or H_2O,SeO_2.—This acid is also produced by dissolving selenion in nitric or nitromuriatic acid. It is deposited from its hot aqueous solution by slow cooling in prismatie crystals like those of saltpetre; but when the solution is evaporated to dryness, the selenious acid is resolved into water and selenious oxide, which sublimes at a higher temperature.

Selenious acid is a very powerful acid, approximating to sulphuric acid in the energy of its reactions. It reddens litmus, decomposes carbonates with effervescence, and decomposes nitrates and chlorides with the aid of heat. Its solution precipitates lead and silver salts, and is decomposed by hydrogen sulphide, yielding a precipitate of selenion sulphide: $H_2SeO_3 + 2H_2S = 3H_2O + SeS_2$.

Selenious acid though the analogue, in regard both to composition and properties, of sulphurous acid, is much more stable than that substanee.

The metallic selenites resemble the sulphites. When heated with sodium carbonate in the inner blow-pipe flame, they emit the characteristic odour of selenion. They are not decomposed by boiling with hydrochloric acid.

Selenic aeid, H_2SeO_4, is analogous in composition to sulphuric acid. The corresponding anhydrous oxide, SeO_3, is not known. Selenie acid is prepared by fusing potassium or sodium nitrate with selenion, precipitating the selenate so produced with a lead salt, and decomposing the resulting compound with hydrogen sulphide. The acid strongly resembles oil of vitriol; but when very much concentrated, it is decomposed by heat into selenious acid and oxygen. The selenates bear the closest analogy to the sulphates in almost every particular. They are decomposed by boiling with hydrochloric acid, with evolution of chlorine and formation of a metallic selenite.

Selenio-sulphuric acid, H_2SeSO_3, corresponding in constitution to thiosulphuric acid, is formed as an alkaline salt by boiling amorphous selenion with an alkaline sulphite. A compound is also known $H_2SeS_2O_6$, corresponding to trithionic acid, $H_2S_3O_6$.

TELLURIUM.

Symbol, Te. Atomic weight, 126 (?). Vapour-density, 126 (?).

This element possesses many of the characters of a metal, but it bears so close a resemblance to selenion, both in its physical properties and its chemical relations, that it is most appropriately placed in the same group with that body. Tellurium is found in a few scarce minerals, in association with gold, silver, lead, and bismuth, apparently replacing sulphur, and is most easily extracted from the bismuth sulpho-telluride of Chemnitz in Hungary. The finely powdered ore is mixed with an equal weight of dry sodium carbonate, and the mixture, made into a paste with oil, is heated to whiteness in a closely covered crucible. Sodium telluride and sulphide are thereby produced, and metallic bismuth is set free. The fused mass is dissolved in water, and the solution freely exposed to the air, when the sodium and sulphur oxidise to sodium hydroxide and thiosulphate, while the tellurium separates in the metallic state.

Tellurium has the colour and lustre of silver; by fusion and slow cooling, it may be made to exhibit the form of rhombohedral crystals, similar to those of antimony and arsenic. It is brittle, and a comparatively bad conductor of heat and electricity; it has a density of 6·26, melts at a little below a red-heat, and volatilises at a higher temperature. Tellurium burns when heated in the air, and is oxidised by nitric acid.

Hydrogen Telluride, H_2Te.—This compound is a gas, resembling hydrogen sulphide and selenide. It is prepared by the action of hydrochloric acid on zinc telluride. It dissolves in water, forming a colourless liquid, which precipitates most metals from their solutions, and deposits tellurium on exposure to the air.

Tellurium Chlorides.—Tellurium forms a dichloride, $TeCl_2$, and a tetrachloride, $TeCl_4$, both volatile and decomposible by excess of water, the latter being completely resolved into tellurous and hydrochloric acids: $TeCl_4 + 3H_2O = 4HCl + H_2TeO_3$.

The tetrachloride unites with the chlorides of the alkali-metals, to form crystallisable double salts.

The *bromides* and *iodides of tellurium* correspond with the chlorides in properties and composition.

Oxides and Oxy-acids of Tellurium.—Tellurium forms two oxides, analogous in composition to the oxides of sulphur, and likewise forming acids by combination with water.

Tellurous Oxide, TeO_2, may be prepared by heating the precipitated acid to low redness. It also separates in semi-crystalline grains from the aqueous solution of the acid when gently heated; more abundantly and in well-defined octahedrons from the solution of tellurous

acid in nitric acid. It is fusible and volatile, slightly soluble in water, but does not redden litmus. When fused with alkaline hydroxides or carbonates, it forms tellurites.

Tellurous Acid, H_2TeO_3, is best obtained by decomposing tellurium tetrachloride with water. It may also be prepared by dissolving tellurium in nitric acid of sp. gr. 1·25, and pouring the solution, after a few minutes, into a large quantity of water. By either process it is obtained as a somewhat bulky precipitate, which, when dried over oil of vitriol, appears as a light, white, earthy mass having a bitter metallic taste. It is slightly soluble in water, more easily soluble in alkalis and acids, the nitric acid solution alone being unstable. Sulphurous acid, zinc, phosphorus, and other reducing agents, precipitate metallic tellurium from the acidified solution of tellurous acid. Like selenious acid, it is decomposed by hydrogen sulphide and alkaline hydrosulphides, with formation of a dark brown tellurium sulphide, TeS_2, which dissolves readily in excess of alkaline hydrosulphide, forming a thiotellurite, M'_2TeS_3.

Tellurous acid is a hydroxide in which the acid and basic tendencies are nearly balanced ; in other words, the tellurium of the compound can replace the hydrogen of an acid to form tellurous salts, and the hydrogen can be replaced by the basylous metals to form metallic tellurites.

Tellurium Salts.		Tellurites.	
$TeCl_4$	Chloride.	H_2TeO_3	Hydrogen tellurite.
$Te(SO_4)_2$	Sulphate.	K_2TeO_3	Potassium tellurite.
$Te(NO_3)_4$	Nitrate.	$HKTeO_3$	Hydrogen and potassium tellurite.
$Te(C_2O_4)_2$	Oxalate. . . .	$H_3K(TeO_3)_2$	Trihydropotassic tellurite.

The tellurites of potassium, sodium, barium, strontium, and calcium are formed by fusing tellurous oxide or acid with the carbonates of the several metals in the required proportions. These tellurites are all more or less soluble in water. The tellurites of the other metals, which are insoluble, are obtained by precipitation.

Compounds of tellurous oxide with the halogen acids are also known. When this oxide is exposed to the action of gaseous *hydrogen bromide* in a vessel cooled to $-14°$, the compound $TeO_2,3HBr$ is formed in groups of small nearly black scales resembling iodine. At 40° this compound gives off HBr, and is reduced to $TeO_2,2HBr$, which, when heated to 300°, is resolved into water and a yellow oxybromide: $TeO_2,2HBr = H_2O + TeOBr_2$; and at a still higher temperature this oxybromide is decomposed into the tetrabromide and tellurous oxide: $2TeOBr_2 = TeBr_4 + TeO_2$. The tetrabromide passes off in black vapours and crystallises on cooling in dark brown needles.

Tellurous oxide is decomposed by *hydriodic acid* at ordinary temperatures, but absorbs it at $-15°$, forming a compound which decomposes as the temperature rises. Tellurous oxide likewise absorbs anhydrous *hydrofluoric acid.*

Telluric Oxide and Acid.—To prepare telluric acid, equal parts of tellurous oxide and sodium carbonate are fused, and the product is dissolved in water; a little sodium hydroxide is added, and a stream of chlorine passed through the solution. The liquid is next saturated with ammonia, and mixed with solution of barium chloride, by which a white insoluble precipitate of barium tellurate is thrown down. This is washed and digested with a quarter of its weight of sulphuric acid, and diluted with water. The filtered solution gives, on evaporation in the air, large crystals of telluric acid, which have the composition, $H_2TeO_4,2H_2O$.

Crystallised telluric acid is freely, although slowly, soluble in water: it has a metallic taste, and reddens litmus paper. The crystals give off their water of crystallisation at 100°, and the remaining acid, H_2TeO_4, when strongly heated, gives off more water, and yields the anhydrous oxide, TeO_3, which is then insoluble in water, and even in a boiling alkaline liquid. At the temperature of ignition, telluric oxide loses oxygen, and passes into tellurous oxide.

The tellurates of the alkali-metals are soluble in water, and are prepared by dissolving the required quantities of telluric acid and an alkaline carbonate in hot water. The other tellurates are insoluble, and are obtained by precipitation.

The composition of the alkaline tellurates is exhibited by the following formulæ :—

Neutral potassic tellurate, ...	K_2TeO_4
Acid or hydro-potassic tellurate, ...	$HKTeO_4$
Superacid or trihydro-potassic tellurate, . .	$HKTeO_4,H_2TeO_4$
Anhydrous quadritellurate, ...	$K_2TeO_4,3TeO_3$.

Tellurium Sulphides.—Tellurium forms two sulphides, TeS_2 and TeS_3, analogous in composition to the oxides; they are obtained by the action of hydrogen sulphide on solutions of tellurous acid and telluric acid respectively. They are brown or black substances, which unite with metallic sulphides, forming salts called thiotellurites and thiotellurates.

NITROGEN COMPOUNDS.

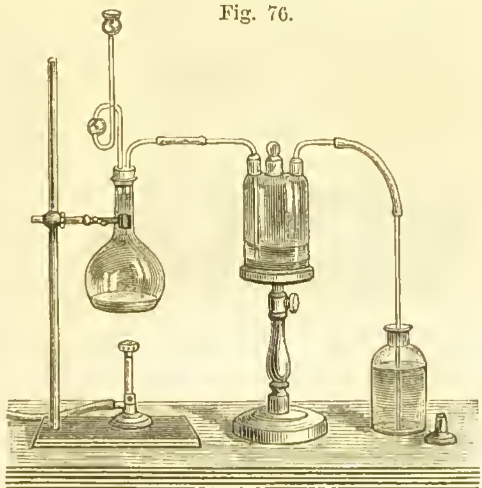
Compounds of Nitrogen and Hydrogen.

Ammonia, NH_3.—This important compound was recognised as a distinct substance by Priestley in 1774, who called it *alkaline air.* It has, however, long been known in the pungent liquid still frequently called *spirit of hartshorn,* which was formerly obtained in an impure state by distilling horn and separating the alkaline watery liquid from the tar which comes over at the same time. The word ammonia is said to be derived from sal-*ammoniac,* so called from the district in Egypt near the temple of Jupiter Ammon, where it was formerly made by heating the soot produced in burning camel's dung.

When powdered sal-ammoniac is mixed with moist calcium hydrate (slaked lime) and gently heated in a glass flask, a large quantity of gaseous matter is disengaged, which, in consequence of its solubility in water, must be collected over mercury, or by displacement, advantage being taken of its relatively low density.

Ammonia thus obtained is a colourless gas; it has a strong pungent odour, and possesses in an eminent degree those properties to which the term *alkaline* is applied; that is to say, it turns the yellow colour of turmeric to brown, that of reddened litmus to blue, and combines readily with acids, neutralising them completely. Ammonia has a density 0·589; a litre weighs 0·7627 gram. Water at 0° and 760 mm. pressure dissolves 1148·8 times its volume of this gas, forming a solution which, in a more dilute state, has long been known under the name of *liquor ammoniæ*; by heat the greater part is again expelled.

Fig. 76.



The aqueous solution of ammonia is prepared as follows:—

Experiment. — Equal weights of sal-ammoniac (NH_4Cl) and quicklime (CaO) are taken; the lime is slaked in a basin, and the salt reduced to powder. These are mixed and introduced into a large flask connected with a wash-bottle and a receiver containing water. The figure shows the arrangement of the apparatus, and the bent tube containing a globule of mercury which acts as a safety-valve. A little water is added to the mixture, just enough to damp it and cause it to aggregate into lumps. On cautiously applying heat to the flask, ammonia is disengaged very regularly

and uniformly, while calcium chloride ($CaCl_2$) and excess of calcium hydroxide (slaked lime) remain in the flask.

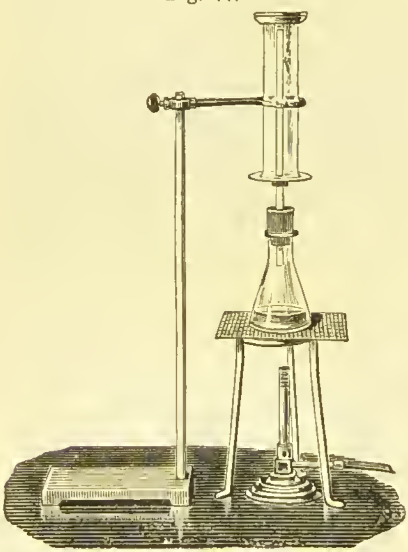
The decomposition of the salt is represented by the equation:

$$2NH_4Cl + Ca(HO)_2 = 2NH_3 + CaCl_2 + 2H_2O.$$

Solution of ammonia should be perfectly colourless, leave no residue on evaporation, and when supersaturated by nitric acid give no cloud or muddiness with silver nitrate. Its density diminishes as its strength increases, that of the most concentrated being about 0·875. The value in alkali of any sample of *liquor ammoniæ* is, however, most safely inferred, not from a knowledge of its density, but from the quantity of acid a given amount will saturate.

When it is desired to examine the properties of the gas, the commercial strong solution of ammonia, which contains about 30 per cent. of its weight of ammonia, forms the most convenient source from which to obtain a supply. It may be collected in a mercurial trough, or more conveniently by displacement of air.

Fig. 77.



Experiment. — Place 3 or 4 ounces of strongest solution of ammonia in a pint flask, fitted with a cork and straight tube, as shown in the figure. The mouth of the jar may be covered with a card in which a slit has been cut to allow the tube to pass. On applying a gentle heat to the solution it speedily boils. When there is a strong smell of the gas outside it may be assumed that the air has been displaced from the jar.

Experiment. — Convey the jar filled with ammonia gas, mouth downwards, into a dish of water. The water rapidly rises, owing to the solubility of the gas.

Experiment.—Dip a piece of litmus paper into dilute sulphuric or hydrochloric acid, and observe that it becomes red. Then hold it in the stream of gas which issues from the tube of the generating flask. The litmus becomes blue.

Experiment.—Collect a jar full of ammonia as already described, and close it by a glass plate greased on the surface to prevent the escape of the gas. Then fill an exactly similar jar with hydrogen chloride gas. Close this also with a glass plate. Then place the two jars mouth to mouth, the hydrogen chloride uppermost, and withdraw the glass covers. The two previously invisible gases unite to form solid white sal-ammoniac or ammonium chloride, NH_3HCl, or NH_4Cl.

When solution of ammonia is mixed with acids, salts are generated exactly analogous to the corresponding potassium and sodium compounds; they will be discussed in connection with the latter. The ammonia salts may be regarded either as direct compounds of ammonia, NH_3, with acids (HCl, for example), or as resulting from the replacement of the hydrogen of an acid by the group NH_4, called *ammonium*, which in this sense is a compound metal, chemically equivalent to potassium, sodium, silver, etc. Thus:

Ammonia	hydrochloride,	NH_3HCl	$= NH_4Cl$	Ammonium	chloride
,,	nitrate,	NH_3,HNO_3	$= NH_4NO_3$	,,	nitrate
,,	sulphate,	$(NH_3)_2H_2SO_4$	$= (NH_4)_2SO_4$	,,	sulphate

The formulæ in the second column are exactly analogous to those of the potassium salts, KCl, KNO_3, K_2SO_4.

The aqueous solution of ammonia may be supposed to contain *ammonium hydroxide*, $NH_4.HO$; but this compound is not known in the solid state.

Any ammoniacal salt can at once be recognised by the evolution of ammonia which takes place when it is heated with slaked lime or solution of potash or soda.

Ammonia is obtainable in very minute quantity by the action of a silent electric discharge upon a mixture of nitrogen and hydrogen gases in the ratio of 1 vol. of the former to 3 vols. of the latter. It may be produced in considerable amount by the action of reducing agents upon nitric acid. Thus, if to a mixture of zinc and dilute hydrochloric acid from which hydrogen is freely escaping, a small quantity of nitric acid is added, the evolution of hydrogen almost ceases, and after a few minutes ammonia may be recognised in the liquid by heating it with excess of potash or soda. Similarly, a solution of a nitrate in caustic soda is reduced by the addition of some aluminium foil, which dissolves in caustic alkali usually with evolution of hydrogen. Ammonia is at once disengaged when a nitrate is present:

$$3NaHO + Al = Na_3AlO_3 + 3H, \text{ and}$$
$$NaNO_3 + 8H = NaHO + NH_3 + 2H_2O\,.$$

Ammonia is also produced by the decomposition of cyanides (see p. 212) by steam, and this reaction has been proposed as a means of utilising the nitrogen of the air for obtaining this compound:

$$\underset{\text{Potassium cyanide.}}{KCN} + 2H_2O = \underset{\text{Potassium formate.}}{KCHO_2} + NH_3.$$

Ammonia is also formed in the putrefaction of animal matters of all kinds.

At the present day the only source of ammonia available practically for manufacturing purposes is the destructive distillation of coal as conducted at the gas works for the purpose of manufacturing coal gas, or in the iron blast furnace, and in coke ovens.

The composition of ammonia may be demonstrated by taking

advantage of the action of chlorine, which combines with the hydrogen and liberates the nitrogen. A glass tube may be used about a yard long, sealed at one end, open at the other, and marked off into three equal portions by rubber rings slipped over it. The tube is filled with chlorine free from air. A tiny tap-funnel is then fitted by means of a rubber stopper to the mouth of the chlorine tube. Strong solution of ammonia is placed in the funnel, and the tap opened for a moment so as to allow a drop of the solution to fall into the chlorine. A flash of greenish light is seen, and white fumes of sal-ammoniac. The remainder of the solution is then admitted drop by drop, avoiding the entrance of air. A gentle heat should be applied to the solution in the tube for a few minutes, in order to complete the decomposition, and the tube is then inverted into a deep jar of water. On opening the tap the water rises and fills two divisions of the tube, leaving one division full of nitrogen gas. Knowing that chlorine combines with an equal volume of hydrogen, and having employed 3 volumes of chlorine, it is obvious that the 1 volume of nitrogen which remains was united in the ammonia with 3 volumes of hydrogen.

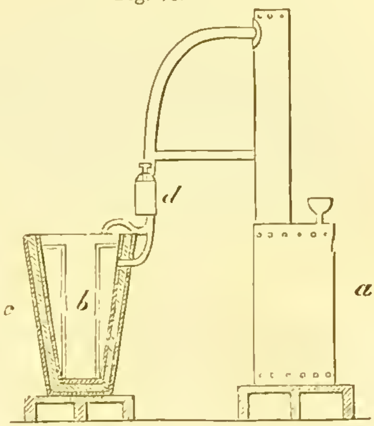
In order to prove that 1 volume of nitrogen, when combined with 3 volumes of hydrogen, constitute 2 volumes of ammonia, recourse may be had to the decomposition of ammonia by heat. When pure ammonia gas confined over mercury is subjected to the action of sparks from an induction coil it is speedily decomposed, and the volume of the gas gradually increases till it is doubled. The resulting gaseous mixture is no longer pungent and soluble in water like ammonia, but is readily inflammable, and can easily be shown to consist of 1 measure of nitrogen with 3 measures of hydrogen. Ammonia is also decomposed into its elements by transmission through a red-hot tube.

Ammonia combines with a number of salts, especially chlorides, forming compounds from some of which it may be disengaged by heat. Taking advantage of this fact, Faraday obtained ammonia in the liquid form by enclosing a quantity of its compound with silver chloride in a strong glass tube, one end of which, containing the salt, could be heated, whilst the opposite end was kept cool. (See fig. 22, p. 51.) At 15° a pressure of between 6 and 7 atmospheres is sufficient to cause it to condense. The compound with calcium chloride may be used in a similar manner. The liquid may also readily be obtained by the use of a strong solution, which, on the application of heat, evolves ammonia nearly free from water vapour. The gas may be made to condense either by the pressure caused by its own accumulation within a sufficiently strong vessel, or by the use of a condensing pump. Liquefied ammonia is extensively used as a means of producing cold, as in the manufacture of ice.

Carré's freezing apparatus consists essentially of a cylindrical boiler *a*, figure 78, holding about two gallons, filled to about three-fourths of its capacity with a strong aqueous solution of ammonia, and connected by pipes with a wrought-iron annular condenser or freezer *c*.

The boiler is first placed over a fire and the freezer in cold water. The boiler is heated to 130° C., whereupon ammonia gas is given off, and condenses in the freezer, together with about one-tenth of its own weight of water. This operation being completed, the boiler is removed from the fire, and immersed in cold water; the freezer, wrapped in dry flannel, is placed outside, and the vessel containing the water to be frozen is placed in the cylindrical space *b*. As the boiler cools, the ammonia gas with which it is filled is redissolved, and the pressure being thus diminished, the ammonia which has been liquefied in *c* is again volatilised, and passes over towards *a*, to redissolve in the water which has remained in the boiler. This rapid evaporation of the ammonia causes a great absorption of heat, whereby the vessel *c* is reduced to a very low temperature, and the water contained in it is frozen. To obtain better contact between the sides of the vessel *b* and the freezer, brine is poured between them. This apparatus gives about 4 lb. of ice an hour, at the price of about a farthing a pound; but large continuously working apparatus are now constructed by which tons of ice can be manufactured at a very low price.

Fig. 78.



Hydrazine, or **Diamidogen**, N_2H_4 or $(NH_2)_2$.—This interesting compound was originally obtained from diazoacetic acid by a complex reaction, which cannot be profitably described in this place.

It is also obtained in the following manner. One of the products of the action of sulphurous acid or acid sulphite of potassium upon potassium nitrite is a compound formerly called potassium sulphazotate $K_2SO_3N_2O_2$, or now potassium dinitroso-sulphonate $KO.SO_2.N(OK)NO$; thus:

$$\underset{\text{Potassium Nitrite.}}{2KONO} + \underset{\text{Potassium Hydrogen sulphite.}}{2KO.SO_2.H} = KOSO_2.N(OK).NO + H_2O + \underset{\text{Potassium sulphate.}}{(KO)_2SO_2}.$$

If this compound, kept cold by ice, is mixed with sodium amalgam, hydrazine sulphonate is formed as the result of the action of nascent hydrogen; thus:

$$KOSO_2.N(OK).NO + 6H = KO.SO_2.NH.NH_2 + H_2O + KHO.$$

The hydrazine remains in solution in the form of sulphate from

which it may be obtained as a volatile hydrate by distillation with caustic potash :

$$KO.SO_2.NH.NH_2 + KOH = K_2SO_4 + NH_2.NH_2.$$

Hydrazine is obtained in the free state with great difficulty. It is a colourless volatile liquid which crystallises at about 0° and boils at 118°. It attacks all kinds of organic matter and even glass. Hence in the free state it can be manipulated only in silver or platinum vessels. It is a powerful base which unites with acids in two proportions, with hydrochloric acid for example it forms the compounds N_2H_4HCl and N_2H_42HCl. It is distinguished from ammonia by its strong reducing action ; thus it throws down a precipitate of cuprous oxide from Fehling's solution of cupric tartrate and a precipitate of metallic silver from ammoniacal silver nitrate. It also decomposes platinic chloride. In all these cases there is an evolution of nitrogen gas.

Hydroxylamine, NH_3O or NH_2OH.—This compound is obtained by the action of nascent hydrogen upon nitric oxide, nitric acid, and some nitrates :

$$HNO_3 + 6H = 2H_2O + NH_3O.$$

It is, however, best prepared from other sources. (*See* "Ammonsulphonic Acids," p. 167.)

Hydroxylamine is a very volatile and easily decomposable base, and can be obtained in the free state only with difficulty. Its salts are decomposed by potash, with evolution of nitrogen and formation of ammonia, quickly in concentrated, gradually in dilute solutions. Solutions of hydroxylamine may, however, be obtained by decomposing the salts in other ways, an alcoholic solution for example, by decomposing the nitrate dissolved in alcohol with alcoholic potash. Alkaline carbonates also separate hydroxylamine, with evolution of carbon dioxide.

Hydroxylamine has been obtained as a crystalline substance, but in this state is very easily decomposed. It melts at about 33°, and may be distilled under much reduced pressure, but if heated under atmospheric pressure it explodes. It is violently and explosively attacked by chlorine which liberates nitrogen and by sodium which liberates hydrogen. On exposure to the air it is rapidly oxidised with production of a nitrite and ammonia.

The solutions have an alkaline reaction, and precipitate many metallic salts ; with the salts of lead, iron, nickel, and zinc, and with chrome alum and common alum, they form precipitates insoluble in excess of hydroxylamine. With aqueous cupric sulphate, hydroxylamine forms a grass-green precipitate, which, when boiled with water, is reduced, with evolution of nitrous oxide gas, to cuprous oxide ; an ammoniacal cupric solution is decolorised by it. Mercuric chloride is reduced to mercurous chloride, and if the hydroxylamine is in excess, to metallic mercury. Silver solutions yield a black pre-

cipitate, which is quickly reduced, with evolution of gas, to metallic silver. Hydroxylamine also reduces acid potassium chromate. In many of these reactions the hydroxylamine appears to be completely decomposed, with formation of nitrogen or its monoxide.

The salts of hydroxylamine decompose, when heated, with copious and sudden evolution of gas. The *hydrochloride*, $NH_3O.HCl$, crystallises from alcohol in long thin prisms; from water in large irregular six-sided tables; it melts at 100°, and then decomposes, with violent evolution of gas, into nitrogen, hydrochloric acid, water, and sal-ammoniac. The *nitrate*, $NH_3O.HNO_3$, solidifies slowly by spontaneous evaporation to a radio-crystalline, very deliquescent mass, easily soluble in absolute alcohol, decomposing at 100°.

A nitro-derivative of hydroxylamine has recently been obtained by the action of ethyl nitrate upon hydroxylamine dissolved in alcohol:

$$\underset{\text{Ethyl nitrate.}}{C_2H_5O.NO_2} + \underset{\text{Hydroxylamine.}}{NH_2OH} = \underset{\text{Alcohol.}}{C_2H_5OH} + \underset{\text{Nitro-hydroxylamine.}}{NH(NO_2)OH}.$$

The new compound acts as a dibasic acid, but is at present known only in the form of its metallic derivatives, the sodium salt having the composition, $Na_2N_2O_3$ (Angeli).

Azoimide.—*Diazoimide, Hydrazoic Acid*, HN_3.—This compound is obtained by various processes, of which the two following are most easily practicable:—

1. Phenyl-diazoimide $C_6H_5N_3$, is first obtained by dissolving phenyl-hydrazine, $C_6H_5HN.NH_2$, in an excess of glacial acetic acid and passing nitrosyl chloride gas into the liquid. The phenyl-diazoimide is separated from the red solution by steam distillation. It is a colourless heavy oil which explodes violently when heated by itself. This is converted into a nitro-compound, $C_6H_4(NO_2)N_3$, by adding it very gradually to about ten times its volume of strong nitric acid contained in a flask. Red fumes are evolved, and when these cease, gentle heat is applied for an hour or two. Water is then added to the solution, and the nitro-compound which is nearly insoluble in water, crystallises out. This compound boiled with alcoholic potash is converted into the potassium salt of azoimide K_3N. In order to carry out the process with the object of preparing the acid for purposes of demonstration, 1 part of the nitro-compound, 1 part of solid caustic potash, and 10 parts by weight of absolute alcohol are boiled together for about an hour in a flask with a Liebig condenser attached vertically to the neck, so that the alcohol as it boils away may return to the flask. Great care must be taken that the residue in the flask does not become dry or it may explode. Excess of dilute aqueous sulphuric acid is then added to the contents of the flask, and the mixture is distilled till about one-fourth has passed over. The distilled liquid is a weak aqueous solution of azoimide.

2. Sodamide, NH_2Na, is first prepared by heating sodium in dry

ammonia. This is best done by placing the metal in several small boats contained in a tube through which ammonia gas is transmitted. This compound is then transformed directly into sodium azoimide, NaN_3, by replacing the stream of ammonia by a current of dry nitrous oxide :

$$NaNH_2 + N_2O = NaN_3 + H_2O.$$

and

$$NaNH_2 + H_2O = NaHO + NH_3.$$

About 50 per cent. of the theoretical yield is obtained. It is important to maintain the temperature during the latter part of the operation between 150° and 250°. If the tube is overheated explosions occur, if not heated sufficiently the decomposition does not proceed. From the resulting sodium salt azoimide may be distilled as described under 1.

Solution of azoimide reddens blue litmus and gives with silver nitrate a white precipitate of silver salt similar in appearance to silver chloride. Neutralised by soda and evaporated to dryness, it yields the corresponding salt, which will bear heating to a somewhat higher temperature than the other salts without risk of explosion.

Azoimide is a colourless liquid boiling at about the same temperature as common ether, that is at 37°, soluble in water and in alcohol, and possessing a strong acid reaction and disagreeable smell. It is most violently explosible on the application of heat or even as a consequence of vibration. It is therefore an extremely dangerous substance to work with. The barium salt, BaN_6, crystallises in hard prisms, the lead salt, PbN_6, in lustrous needles which are easily soluble in water. The silver salt, AgN_3, is also crystallisable, but being very slightly soluble in water, is usually precipitated as a white precipitate resembling the chloride of silver, but differing from that compound in being unaffected by light and in being violently explosible on heating or by friction.

Compounds of Nitrogen with the Halogen Elements.

Nitrogen Trichloride, NCl_3.—When sal-ammoniac or ammonia nitrate is dissolved in water, and a jar of chlorine is inverted in the solution, the gas is absorbed, and a deep yellow oily liquid is observed to collect upon the surface of the solution, ultimately sinking in globules to the bottom. This is nitrogen chloride, one of the most dangerously explosive substances known.

The change may be explained by the equation :

$$NH_4Cl + 3Cl_2 = NCl_3 + 4HCl.$$

Nitrogen chloride is very volatile, and its vapour is exceedingly irritating to the eyes. It has a sp. gr. 1·653. It may be distilled at 71°, although the experiment is attended with great danger.

Between 93° and 105° it explodes with fearful violence. Contact with almost any combustible matter, as oil or fat of any kind, determines the explosion at common temperatures, a vessel of porcelain, glass, or even of cast-iron, being broken by it to pieces, and a leaden cup receiving a deep indentation.

Nitrogen Tribromide, NBr_3.—This compound is formed by the action of potassium bromide on the trichloride.

Nitrogen and Iodine.—When alcoholic solution of iodine is added to caustic ammonia, a black powder, called nitrogen iodide, is precipitated. The solid filtered from the brown solution should be distributed while still wet in small quantities upon separate pieces of bibulous paper, and left to dry in the air.

Nitrogen iodide is a black insoluble powder, which, when dry, explodes with the slightest touch—even that of a feather—and sometimes without any obvious cause. The explosion is, however, not nearly so violent as that of nitrogen chloride, and is attended with the production of violet fumes of iodine. According to Gladstone, this substance contains hydrogen, and may be viewed as NHI_2, that is, as ammonia in which two-thirds of the hydrogen are replaced by iodine. It appears, however, that the substance called nitrogen iodide varies in composition, for, by changing the mode of preparation, several compounds containing the elements of nitrogen tri-iodide with ammonia may be obtained.

Compounds of Nitrogen and Oxygen.

There are five distinct compounds of nitrogen and oxygen, thus named and constituted :—

		Composition.			
		By weight.		By volume.	
	Formula.	Nitrogen.	Oxygen.	Nitrogen.	Oxygen.
Nitrous Oxide, .	. N_2O	28	16	. 2	1
Nitric Oxide, .	. NO	14	16	1	1
Nitrous Anhydride,	. N_2O_3	28	48	2	3
Nitric Peroxide,	. N_2O_4	28	64	2	4
	or NO_2	14	32	1	2
Nitric Anhydride,	. N_2O_5	28	80	2	5

A comparison of these numbers will show that the quantities of oxygen which unite with a given quantity of nitrogen are to one another in the ratio of the numbers 1, 2, 3, 4, 5.

Compounds called respectively hyponitrites, nitrites, and nitrates, are known which contain the elements of the first, third, and fifth of these oxides in union with the elements of metallic oxides. The hydrogen salts are also called hyponitrous, nitrous, and nitric acid.

The composition of these acids and of their potassium salts is represented by the following formulæ :

Hydrogen Hyponitrite, of Hyponitrous acid,	HNO or $H_2N_2O_2$
Potassium Hyponitrite, ...	KNO or $K_2N_2O_2$
Hydrogen Nitrite, or Nitrous acid, . .	HNO_2
Potassium Nitrite, ...	KNO_2
Hydrogen Nitrate, or Nitric acid, . .	HNO_3
Potassium Nitrate, ...	KNO_3

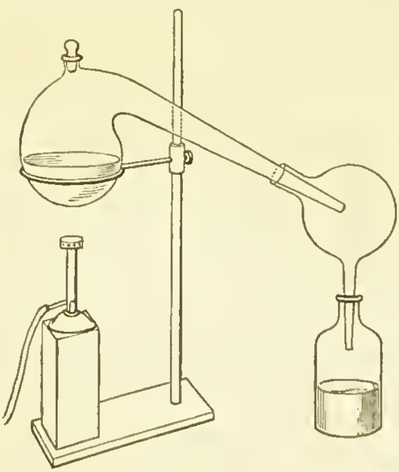
Nitric oxide does not form salts with metallic oxides. Nitric peroxide produces nitrite and nitrate simultaneously.

It will be convenient to commence the description of these compounds with the last on the list, viz., the nitrates, inasmuch as they are the sources from which all the other compounds in the series are obtained.

Nitric Acid, HNO_3.—In certain parts of India, and in other hot dry climates, the surface of the soil is occasionally covered by a saline efflorescence, like that sometimes seen on newly plastered walls ; this substance collected, dissolved in hot water, and crystallised from the filtered solution, furnishes the highly important salt known in commerce as nitre or saltpetre, and consisting of potassium nitrate.

Experiment.—To obtain nitric acid, equal weights of powdered nitre (30–40 grams) and strong sulphuric acid are introduced into a glass retort connected with a receiver, and gentle heat is applied. The arrangement is shown in the accompanying figure. No corks or luting of any kind must be used. As the distillation advances, the red fumes which first arise disappear, but towards the end of the process they again become manifest. When this happens, and very little liquid passes over, while the greater part of the saline matter of the retort is in a state of tranquil fusion, the operation may be stopped ; and when the retort is nearly cold, water may be introduced to dissolve out the saline residue.

Fig. 79.



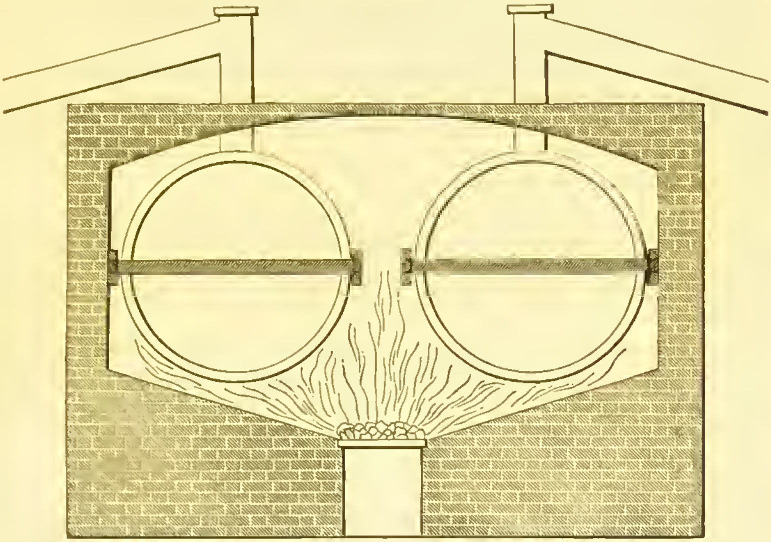
The reaction consists in an interchange between the potassium of the nitrate and half the hydrogen of the sulphuric acid (hydrogen sulphate), whereby there are formed hydrogen nitrate which

distils over, and hydrogen and potassium sulphate which remains in the retort:

$$KNO_3 + H_2SO_4 = HNO_3 + HKSO_4.$$

In the manufacture of nitric acid on the large scale, the glass retort is replaced by a cast-iron cylinder, and the receiver by a series of earthen condensing vessels connected by tubes, as shown in the

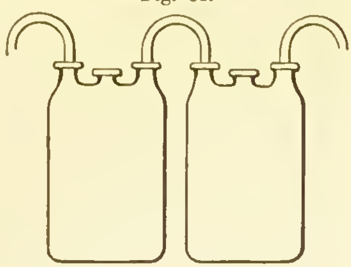
Fig. 80.



accompanying figures. Sodium nitrate, found native in Peru, is generally substituted for the more costly potassium nitrate.

Pure nitric acid, in its most concentrated form, is obtained by mixing the product thus obtained with about an equal quantity of strong sulphuric acid, redistilling, collecting apart the first portion which comes over, and exposing it, in a vessel slightly warmed and sheltered from the light, to a current of dry air made to bubble through it, which completely removes the nitrous acid. In this state the product is colourless; it has the sp. gr. 1·517 at 15·5°, and boils at 84·5°.

Fig. 81.



On boiling nitric acid of different degrees of concentration, at the ordinary atmospheric pressure, a residue is left, boiling at 120·5° and 760 mm. barometer, having the sp. gr. 1·414 at 15·5°, and containing about 69 per cent. of real nitric acid, HNO_3, with 31 per cent. of water. This acid was formerly supposed to be a definite compound

of nitric acid with water; but Roscoe has shown that this assumption is incorrect, the composition of the acid varying according to the pressure under which the liquid boils.

The acid prepared in the way described is apt to contain traces of chlorine from common salt in the nitre, and sometimes of sulphate from accidental splashing of the pasty mass in the retort. To discover these impurities, a portion is diluted with four or five times its bulk of distilled water, and divided between two glasses. Solution of silver nitrate is dropped into the one, and solution of barium nitrate into the other; if no change ensue in either case, the acid is free from the impurities mentioned.

Nitric acid is exceedingly corrosive, staining the skin deep yellow, acting violently upon many metals and upon organic substances. The rate of action and the nature of the products depend in some degree upon its state of concentration. Its chief reactions may be classified under three heads.

First, it behaves with metallic oxides as acids usually do, exchanging its hydrogen for an equivalent quantity of metal and forming salts. The nitrates are remarkable for being all soluble in water, with the exception of a few basic salts such as those of bismuth.

Secondly, it easily parts with a portion of its oxygen, and thus acts the part of a powerful oxidising agent. Hence in its action upon metals hydrogen is never evolved, for the hydrogen displaced by the metal is converted into water, and a mixture of the lower oxides of nitrogen usually escapes in the form of gas.

Thirdly, the action of pure undiluted nitric acid upon carbo-hydrogen compounds often results in the exchange of a portion of the hydrogen for the elements of nitric peroxide, NO_2. This action is not accompanied by the evolution of gas, water being the only other product. The compounds thus formed are called nitro-compounds; one of the best examples is nitro-benzene, $C_6H_5(NO_2)$, formed from benzene, C_6H_6, by the exchange of an atom of hydrogen for one nitro-group.

The chief characters of nitric acid may be illustrated by such experiments as the following:—

Experiments.—1. Place about half an ounce of nitric acid in an evaporating dish and pour into it, with constant stirring, ordinary solution of potash till, on placing a drop of the liquid upon blue litmus paper, it produces only slight redness. Then evaporate to about one-fourth of its bulk and let the liquid cool. Crystals of potassium nitrate will be deposited. If no crystals are found when the liquid is quite cold, evaporate a little further.

2. Place in separate test-tubes small pieces of copper, zinc, tin, and platinum (foil). Pour into each sufficient strong nitric acid (commercial, density 1·42) to cover the metal. The platinum remains unacted upon even when the acid is boiled. The other metals are attacked with violent evolution of red gas; the copper yielding a blue solution of copper nitrate, the zinc colourless zinc nitrate, while

the tin gives an insoluble white powder, consisting of the dioxide, SnO_2, in combination with water.

3. Repeat the experiment with copper, using nitric acid previously diluted with an equal volume of water. The action is less violent, and the gas evolved consists chiefly of colourless nitric oxide. The action may be expressed in two stages thus—

$$x[Cu + 2HNO_3 = Cu(NO_3)_2 + 2H].$$

Then, if the acid is concentrated, the hydrogen partly reduces another portion of the nitric acid to nitric peroxide :

$$2HNO_3 + 2H = 2H_2O + N_2O_4.$$

If the acid is somewhat diluted, the reduction goes further and nitric oxide is formed :

$$2HNO_3 + 6H = 4H_2O + 2NO.$$

4. Place in another test-tube some granulated zinc, cover it with water, and add a few drops of nitric acid so that only very slight action is visible. After some time ($\frac{1}{4}$ hour) pour the solution into a flask, add excess of solution of potash and heat. Ammonia is evolved, and may be recognised by the nose or by the use of a piece of red litmus paper. In this case part of the nitric acid is not only deprived of oxygen, but is supplied with additional hydrogen.

$$\begin{aligned} 2[Zn + 2HNO_3 &= Zn(NO_3)_2 + 2H] \\ HNO_3 + 8H &= H_3N + 3H_2O. \end{aligned}$$

5. Place a little powdered charcoal on a piece of sheet iron. Make it warm over a lamp placed in a fume chamber, then pour on a little concentrated nitric acid. The charcoal burns.

6. Mix in a large test-tube or small beaker, standing in a basin of cold water, about an ounce of commercial strong nitric acid with half its volume of strong sulphuric acid. When the mixture is cold, add pure benzene, *drop by drop*, as long as it is dissolved. Then pour the solution into a large beaker full of cold water. A yellow heavy oil separates, having a strong odour of essential oil of almonds. This compound is called nitro-benzene or nitro-benzol, and is extensively used for scenting soap and for other purposes. Its formation from benzene is represented by the following equation :

$$HNO_3 + C_6H_6 = H_2O + C_6H_5NO_2.$$

Nitric acid acts in a somewhat similar manner upon many other carbo-hydrogen compounds. Thus, if clean cotton wool be immersed in such a mixture of nitric and sulphuric acids, hydrogen is exchanged for the nitro group, and the cotton, though unaltered in appearance, increases in weight and acquires new properties. After soaking in the acid a few minutes, the cotton should be removed and thoroughly washed with water till entirely free from acid. If it is then dried in a steam oven at the temperature of boiling water, it

will be found that the cotton on the application of a flame disappears with a bright flash. This is the substance known as gun-cotton, now extensively used as an explosive. This compound is derived from cellulose, the material of which cotton consists, $(C_6H_{10}O_5)_n$, by the substitution of $(NO_2)_3$ for H_3, thus $(C_6H_7(NO_2)_3O_5)_n$. This compound, however, is not rightly to be viewed as a nitro-compound, as it has the constitution and chemical properties of a nitrate.

Nitric acid is not so easily detected in solution in small quantities as many other acids. Owing to the solubility of all its compounds, no *precipitant* can be found for this acid. A good mode of testing it is based upon its power of bleaching a solution of indigo in sulphuric acid when boiled with that liquid. The absence of chlorine must be insured in this experiment; otherwise the result will be equivocal.

The best method for the detection of nitric acid is the following:—

Experiment.—The substance to be examined is dissolved in a small quantity of water, and the solution cautiously mixed with an equal volume of concentrated sulphuric acid; the liquid is then left to cool, and a strong solution of ferrous sulphate carefully poured upon it, so as to form a separate layer. If large quantities of nitric acid are present, the surface of contact first, and then the whole of the liquid, becomes black. If but small quantities of nitric acid are present, the liquid becomes reddish-brown or purple. The ferrous sulphate reduces the nitric acid to nitric oxide, which, dissolving in the solution of ferrous sulphate, imparts to it a dark colour.

Nitrogen Pentoxide, or Nitric Anhydride, N_2O_5.—This compound was discovered in 1849 by Deville, who obtained it by exposing silver nitrate to the action of chlorine gas. Chlorine and silver then combine, forming silver chloride, which remains in the apparatus, while oxygen and nitrogen pentoxide volatilise:

$$2AgNO_3 + Cl_2 = 2AgCl + N_2O_5 + O.$$

It may also be prepared by slowly distilling pure and highly concentrated nitric acid at about 37° with phosphoric oxide, a substance which has a very powerful attraction for water. The distillate consists of two layers of liquid, the upper of which is nitrogen pentoxide mixed with nitrous and nitric acids; and on cooling this upper layer with ice, the pentoxide separates in crystals.

Nitrogen pentoxide is a colourless substance, crystallising in six-sided prisms, which melt at 30° and boil between 45° and 50°, when they begin to decompose. Its density in the solid state is above 1·64; in the liquid state below 1·636. Nitrogen pentoxide explodes when suddenly heated, and at the ordinary temperature slowly decomposes. It dissolves in water with great rise of temperature, forming hydrogen nitrate or nitric acid. It also unites with a smaller proportion of water, forming the *hemihydrate* $2N_2O_5.H_2O$, which constitutes the chief part of the lower layer of the distillate obtained in the manner just described. It is liquid at ordinary temperatures but crystallises in a freezing mixture.

Aqua Regia.—This name is given to a mixture of nitric and hydrochloric acids, which has long been known for its property of dissolving gold and platinum. When heated it gives off nitrosyl chloride (p. 164) and free chlorine, the latter of which attacks any metal that may be present, forming usually the highest chloride the metal is capable of forming :

$$NO_3H + 3HCl = 2H_2O + NOCl + Cl_2.$$

Nitrogen Monoxide, or **Nitrous Oxide,** N_2O (*Laughing Gas*).—When solid ammonium nitrate is heated, it is resolved into water and nitrogen monoxide : $NH_4NO_3 = 2H_2O + N_2O$.

Experiment.—The apparatus used in preparing ammonia from sal-ammoniac and lime may be used (p. 147). The washing bottle should be empty, or may be dispensed with altogether. Place in the flask an ounce or two of solid ammonium nitrate, heat it gently at first till it melts, then raise the temperature till it boils steadily. Collect the gas in jars in a trough filled with warm water. Avoid heating the salt very strongly.

Nitrogen monoxide is a colourless, transparent, and almost inodorous gas, of distinctly sweet taste. Its density is 1·525 ; a litre of it weighs 1·9717 gram ; 100 cubic inches weigh 47·29 grains. It supports the combustion of a taper or a piece of phosphorus with almost as much energy as pure oxygen : it is easily distinguished, however, from that gas by its solubility in cold water, which dissolves nearly its own volume : hence it is necessary to use tepid water in the pneumatic trough or gas-holder, otherwise great loss of gas will ensue.

Experiments.—1. Plunge a lighted taper into a jar of nitrous oxide and notice the brilliancy of the flame.

2. Take a chip of wood, ignite it, then blow out the flame, leaving the charred extremity red hot. Now, plunge this quickly into nitrous oxide : the wood is rekindled, though less energetically than when pure oxygen is used.

3. Collect some of the gas in a test-tube. Close the mouth of the tube with the thumb so as to retain a little water with the gas. Shake them well together, then immerse the tube in cold water, remove the thumb for a moment to admit more water and close the tube again and shake, repeating the same operations several times. The gas, if pure, will be entirely absorbed.

Gaseous nitrogen monoxide mixed with an equal volume of hydrogen, and fired by the electric spark in the eudiometer, explodes with violence, and liberates its own measure of nitrogen. Every two volumes of the gas must consequently contain two volumes of nitrogen and one volume of oxygen, the whole condensed or contracted one-third—a constitution resembling that of vapour of water.

A remarkable property of this gas is its power of producing insensibility when inhaled. If quite pure, or merely mixed with atmospheric air, it may be respired for a short time without danger

or inconvenience. The effect is very transient, and is not followed by depression. The gas is much used as an anæsthetic in dental surgery.

Nitrogen monoxide is liquefied by a pressure of 50 atmospheres at 45° F. (7·2° C.); the liquid monoxide has a density 0·9004, and, under a pressure of 763 mm., boils at −87·9°; it is not miscible with water. Faraday solidified it by exposing it in a sealed tube to the cold produced by a mixture of solid carbon dioxide and ether, but he supposed that it could not be solidified by the cold produced by its own evaporation. This, however, may be effected if the evaporation be accelerated by a strong current of air. A very fine steel tube is directed into the axis of a thin brass cone, having a small opening, about the eighth of an inch, at its apex. On causing a stream of the liquid to issue from the jet, it is retained in the cone for a moment, and then forcibly blown out at the apex, together with a strong stream of air. The solid is in this way formed in some quantity, and may be collected in a dish lined with filter-paper, or other suitable vessel. Solid nitrogen monoxide is more compact in appearance than solid carbon dioxide, and, unlike the latter, it melts and boils, if gently warmed, before passing into the gaseous state: hence if placed in contact with the skin, it produces a painful blister, like a burn.

Hyponitrites, $(MNO)_n$.—When a solution of sodium nitrate, $NaNO_3$, or ammonium nitrate, NH_4NO_3, is treated with sodium amalgam, the nitrate gives up 2 atoms of oxygen to the sodium, and is reduced to hyponitrite. On neutralising the excess of alkali in the liquid by acetic acid a solution of sodium hyponitrite is obtained, which gives with silver nitrate a yellow precipitate of silver hyponitrite. The acid corresponding to these salts has not been isolated, as it appears to be too unstable to exist at common temperatures. When the original alkaline liquid is acidified with acetic acid, and heated, the hyponitrous acid is resolved into water and nitrogen monoxide, which escapes as gas: $2HNO = H_2O + N_2O$.

There is some reason to believe that the formula should be written $H_2N_2O_2$.

Nitric Oxide, NO.—This gas is the chief product of the action of slightly diluted nitric acid upon metals, especially copper and mercury. The action has already been explained under nitric acid. When copper is used the initial and final stages of the process may be represented by the equation:

$$8HNO_3 + 3Cu = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

The gas obtained by this method is, however, not quite free from other oxides of nitrogen, and even nitrogen itself. The amount of these secondary products increases towards the end of the process, when a considerable quantity of copper nitrate has accumulated in the liquid. To obtain pure nitric oxide advantage is taken of the

fact that it forms a compound with ferrous sulphate, which is decomposed by boiling. A mixture of ferrous sulphate, nitre, and water acidified with sulphuric acid gives off pure nitric oxide, while ferric sulphate remains in solution :

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 4H_2O + 2NO.$$

Experiment.—Clippings or turnings of copper are put into the apparatus employed for preparing hydrogen (p. 23), together with a little water, and nitric acid is added by the funnel until brisk effervescence is excited. The gas may be collected over cold water, as it is not sensibly soluble.

Experiments.—The gas obtained in this manner is colourless and transparent : (1) Mixed with air or oxygen gas it produces deep red fumes, which are readily absorbed by water : this character is sufficient to distinguish it from all other gaseous bodies. (2) A lighted taper plunged into the gas is extinguished. (3) Lighted phosphorus, however, burns in it with great brilliancy.

The density of nitric oxide is 1·04 when air is unity, or 15 if compared with hydrogen ; a litre weighs 1·3434 gram. The relative density of nitric oxide gas is not altered even at the temperature of $-100°$; hence the molecular weight of the gas is under no circumstances greater than 30, and the formula must be written NO, and not as formerly N_2O_2. The boiling point of liquid nitric oxide is about $-154°$. Nitric oxide contains equal measures of oxygen and nitrogen gases united without condensation. When this gas has passed into the solution of a ferrous salt, it is absorbed in large quantity, and a deep brown, or nearly black liquid produced, which seems to be a definite compound of the two substances. The compound is decomposed by boiling. Nitric oxide unites with half its volume of chlorine, producing nitrosyl chloride, NOCl.

Nitrogen Trioxide, or **Nitrous Anhydride,** N_2O_3.—When four measures of nitric oxide are mixed with one measure of oxygen, and the gases, perfectly dry, are exposed to a temperature of $-18°$, they condense to a thin mobile blue liquid, which emits orange-red vapours.

Nitrogen trioxide is most readily obtained by pouring concentrated nitric acid on lumps of arsenious acid, and gently warming the mixture, in order to start the reaction. The orange-red gas then evolved is a mixture of equal volumes of NO and NO_2, which unite at low temperatures, forming a blue liquid.

Nitrous Acid, HNO_2, is obtained as a beautiful blue solution on dissolving the trioxide in ice-cold water : $N_2O_3 + H_2O = 2HNO_2$. It is very unstable, even at ordinary temperatures, decomposing into nitric acid, nitric oxide, and water, $3HNO_2 = HNO_3 + 2NO + H_2O$. In consequence of this instability of the acid, the metallic nitrites cannot be obtained pure by treating the aqueous solution of the acid with metallic oxides. They may be formed in other

ways: potassium nitrite, for example, may be obtained by fusing the corresponding nitrate, whereby a third part of the oxygen is driven off; and a solution of potassium or sodium nitrite may be prepared by passing the mixed gases—obtained as above by heating nitric acid with arsenious oxide (or with starch)—into a solution of caustic potash or soda.

Nitrosyl Chloride, or Nitrous Chloride, NOCl.—This is the only known oxy-chloride of nitrogen. It is formed by direct union of chlorine and nitric oxide, and by the action of phosphorus pentachloride on potassium nitrite: $PCl_5 + NO.OK = NO.Cl + KCl + POCl_3$; also, together with free chlorine, when a mixture of nitric and hydrochloric acids (*aqua regia*) is slowly heated:

$$HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O.$$

It is most easily procured by the action of nitrosyl hydrogen sulphate (*q.v.*) on dry common salt:

$$NOHSO_4 + NaCl = NOCl + NaHSO_4.$$

Nitrosyl chloride in the pure state is an orange-yellow gas, which, in a freezing mixture, condenses to a deep orange-coloured limpid liquid, boiling at about $-8°$. It is a very stable compound, and is not decomposed at any temperature short of a red-heat. It unites with many metallic chlorides, and is decomposed by basic oxides and by water, yielding a nitrite and a chloride: *e.g.*,

$$NOCl + 2KOH = KNO_2 + KCl + H_2O.$$

Nitrosyl Bromide, NOBr, formed by passing nitric oxide into bromine at $-7°$ to $-15°$, is a blackish-brown liquid, which begins to decompose at $-2°$, giving off nitric oxide. If the temperature is allowed to rise to $+20°$, a dark brownish-red liquid remains, consisting of *nitrosyl tribromide*, $NOBr_3$, which is also formed when bromine is saturated with nitric oxide at ordinary temperatures. It is said to volatilise undecomposed when quickly heated, but is resolved by slow heating into bromine and nitric oxide.

Nitrogen Peroxide, N_2O_4 or NO_2.—This is the principal constituent of the deep red fumes always produced when nitric oxide escapes into the air, and during the action of nitric acid on metals. It is the only coloured gaseous oxide of nitrogen, for nitrogen trioxide is completely decomposed when converted into vapour.

It may be obtained in the pure state:—(1) By exposing a mixture of 2 vols. nitric oxide and 1 vol. oxygen, both thoroughly dried, to the action of a freezing mixture of salt and ice; the tetroxide then condenses in transparent crystals, or if the slightest trace of moisture is present, into yellowish or greenish liquid. (2) By the direct combination of oxygen with the trioxide, as when a stream of oxygen is passed into the mixture of oxides of nitrogen evolved by the action of fuming nitric acid on arsenious acid. (3) By heating thoroughly

dried lead nitrate in a retort, whereby a mixture of the tetroxide and oxygen is evolved, the former of which may be condensed as above, while the latter passes on :

$$(NO_3)_2Pb = PbO + O + N_2O_4.$$

The first portions of nitrogen tetroxide thus obtained do not solidify, doubtless owing to the presence of a trace of moisture ; but if the receiver be changed in the midst of the operation, and if care has been taken to avoid moisture, the later portions may be obtained in the crystalline form.

Nitrogen tetroxide at very low temperatures forms transparent, colourless, prismatic crystals which melt at $-9°$, but when once melted do not resolidify till cooled down to $-30°$. Above $-9°$ it forms a mobile liquid of density 1·45, the appearance of which varies greatly according to the temperature. When still liquid below $-9°$ it is almost colourless; at $-9°$ it has a perceptible greenish-yellow tint ; at 0° the colour is somewhat more marked ; at $+10°$ it is decidedly yellow ; and at 15° and upwards, orange-yellow, the depth of colour increasing progressively with temperature up to 22°, the boiling point of the liquid. The vapour has a brown-red colour, the depth of which also increases with the temperature, until at 40° it is so dark as to be almost opaque. This remarkable change of colour is accompanied by a great diminution of density as the temperature rises, both phenomena pointing to a molecular change produced in the vapour by heat. Playfair and Wanklyn determined the density of the vapour by Dumas' method, using nitrogen as a diluent, and found the densities at different temperatures as follows :—

Temperature.	Vapour-density.
97·5°,	1·783
24·5,	2·520
11·3,	2·655
4·2,	2·588

There can be no doubt that these changes of density correspond to changes in the molecular constitution of the compound. At low temperatures it consists almost entirely of molecules having the composition of the tetroxide, N_2O_4, which would require a density of 3·2. If the temperature is raised, these are broken into simpler groups,

$$N_2O_4 = 2NO_2,$$

and when the decomposition is complete, the gas has a density 1·6, as compared with air at the same temperature. (*See* "Dissociation.")

At a temperature just below redness the dark red gas becomes colourless, being resolved into nitric oxide and oxygen,

$$NO_2 = NO + O.$$

These changes occur in reverse order on allowing the gas to cool.

The vapour is absorbed by strong nitric acid, which thereby acquires a yellow or red tint, passing into green, then into blue, and afterwards disappearing altogether on the addition of successive portions of water. The deep red fuming acid of commerce, called *nitrous acid*, is simply nitric acid impregnated with nitrogen tetroxide.

Nitrogen tetroxide is decomposed by water at low temperatures in such a manner as to yield nitric and nitrous acids: $N_2O_4 + H_2O = HNO_3 + HNO_2$; but when added to excess of water at ordinary temperatures, it yields nitric acid and the products of decomposition of nitrous acid, namely, nitric acid and nitric oxide. In like manner, when passed into alkaline solutions, it forms a nitrate and a nitrite of the alkali-metal.

Nitrogen Sulphide, N_2S_2, is obtained, together with other compounds, by the action of dry ammonia on sulphur protochloride (p. 125), or on thionyl chloride (p. 139), as a yellow powder which crystallises from carbon sulphide in yellowish-red rhombic prisms. It becomes dark coloured at 120°, and emits pungent vapours; sublimes at 135° in yellowish-red crystals; begins to melt and give off gas at 158°; decomposes rapidly at 160°, and detonates violently when struck.

Dinitrososulphonates, $M_2SO_3(NO)_2$.—The acid is not known, but the alkali-salts are formed on passing nitric oxide into the solution of an alkaline sulphite, or by the action of sulphurous acid on a solution of a nitrite. They are colourless and crystalline, and are decomposed by all acids, even by carbonic acid, into sulphates and nitrogen monoxide, $K_2SO_3(NO)_2 = K_2SO_4 + N_2O$. The potassium salt is resolved by heat into potassium sulphite, K_2SO_3, and nitric oxide, NO.

Nitrosyl Hydrogen Sulphate, $NOHSO_4$ or $NO_2.SO_2.OH$.—This is the composition of the lead-chamber crystals, formed during the manufacture of sulphuric acid, when the supply of steam is insufficient to form that acid at once (p. 133). The same compound is formed by the action of strong nitric acid on sulphurous oxide:

$$SO_2 + NO_2.OH = NO_2.SO_2.OH;$$

by passing vapour of nitrosyl chloride, evolved together with chlorine from *aqua regia*, into sulphuric acid:

$$NOCl + HO.SO_2.OH = HCl + NO_2.SO_2.OH;$$

and together with nitric acid by the action of nitrogen tetroxide on sulphuric acid:

$$N_2O_4 + HO.SO_2.OH = NO_2.OH + NO_2.SO_2.OH.$$

It crystallises in rhombic prisms, or in tabular or nodular masses,

which begin to melt and give off vapour at 30°. It dissolves in small quantities of cold water, forming a blue liquid containing sulphuric and nitrous acids: $NO_2.SO_2.OH + HOH = HO.SO_2.OH + NO_2H$. It dissolves also in strong sulphuric acid, forming a solution which can be distilled without decomposition.

Nitrosyl Pyro-sulphate, $(NO)_2S_2O_7$, is formed by the action of heat on the foregoing compound, but is best prepared by passing dry nitric oxide into sulphuric oxide, and heating the resulting solution nearly to the boiling point: $3SO_2O + 2NO = (NO_2.SO_2)_2O + SO_2$. It is also formed by the action of sulphurous oxide on nitrogen tetroxide, and by heating the componnd mentioned below. It crystallises in hard colourless square prisms, melting at 217° to a yellow liquid which becomes darker at a higher temperature, and distils unchanged at 360°. It dissolves readily in strong sulphuric acid, forming nitrosyl hydrogen sulphate.

A compound having the composition $(NO_2SO_3)_n$, is formed when sulphuric oxide and nitrogen tetroxide are brought together at a low temperature, and separates as a white crystalline mass, which gives off oxygen when heated, and is reduced to the preceding compound.

Ammon-Sulphonates.

The names sulphonic acid and sulphonate are applied to derivatives of unsymmetrical sulphurous acid, $H.SO_2.OH$, formed by replacing the first hydrogen atom by a radicle of equivalent combining capacity, *e.g.*, methyl sulphonic acid, $CH_3.SO_2.OH$, etc.

The following compounds therefore must be regarded as having been formed from ammonia by the replacement of successive atoms of hydrogen by the group of atoms SO_3H or SO_3K. Thus:

Ammonia, ...	NH_3
Ammon-sulphonic acid, . . .	$NH_2(SO_3H)$
Ammon-disulphonic acid, . . .	$NH(SO_3H)_2$
Ammon-trisulphonic acid, . . .	$N(SO_3H)_3$.

Similarly the hydroxylamine derivatives contain HO in place of H in the molecule of ammonia.

Hydroxylamine, ...	$NH_2(HO)$
Hydroxylamine disulphonic acid or Hydroxy-ammon-disulphonic acid, ...	$N(SO_3H)_2(OH)$.

Potassium nitrilosulphonate, or *ammon-trisulphonate*, $N(SO_3K)_3.2H_2O$, is obtained as a crystalline precipitate on adding potassium sulphite in excess to a solution of potassium nitrite (Raschig):

$$3K_2SO_3 + KNO_2 + 2H_2O = N(SO_3K)_3 + 4KHO.$$

By prolonged contact with water, or by boiling the solution, this salt yields a mixture of acid potassium sulphate and the following.

Potassium imido-sulphonate, or *ammon-disulphonate*, $NH(SO_3K)_2$. This compound is best prepared by moistening the foregoing salt with a little very dilute sulphuric acid, leaving it for a day, then washing it with cold water and crystallising from a slightly ammoniacal solution. When mixed with the calculated quantity of potash it yields large easily soluble crystals of a basic compound, $NK(SO_3K)_2.H_2O$. By adding mercuric chloride to a solution of this salt, a remarkable mercuric compound, $Hg[N(SO_3K)_2]4H_2O$, is obtained.

Potassium amido-sulphonate, or *ammon-sulphonate*, $NH_2(SO_3K)$. When the preceding tri- or disulphonates are boiled with water they yield acid solutions, for example :

$$N(SO_3K)_3 + 2H_2O = NH_2(SO_3K) + 2KHSO_4 .$$

The liquid is neutralised, with chalk, filtered, and evaporated. After the calcium and potassium sulphates have crystallised out, the solution yields very soluble crystals of potassium ammon-sulphonate. From this the acid, $NH_2.SO_3H$, may be obtained. It is a stable crystalline substance.

Potassium - hydroxylamine - disulphonate, $N(OH)(SO_3K)_2.2H_2O$. Sodium nitrite dissolved in ice-cold water is mixed with sodium hydrogen sulphite in the proportions required by the equation—

$$NaNO_2 + 2NaHSO_3 = N(OH)(SO_3Na)_2 + NaHO .$$

A cold saturated solution of potassium chloride is then added, and after some hours the potassium hydroxylamine-disulphonate crystallises out. This compound is very unstable, being easily resolved into potassium sulphate and *hydroxylamine-monosulphonate*, $N(OH)H(SO_3K)$. This last in its turn, by boiling with water, yields hydroxylamine and potassium sulphates.

An easy process for the production of hydroxylamine, therefore, consists in boiling the hydroxylamine-disulphonate with water for some hours.

$$2N(OH)(SO_3K)_2 + 4H_2O = (NH_3OH)_2SO_4 + 2K_2SO_4 + H_2SO_4 .$$

From this the potassium sulphate may be removed by crystallisation, and the hydroxylamine salt prepared from the mother liquids.

By the action of sulphurous acid or of sulphites upon a strongly alkaline solution of nitrite, may be obtained another series of salts derived from the hypothetical dihydroxylamine, $NH(OH)_2$, together with more complex compounds containing 2 atoms of nitrogen, such as the sulphazotates already referred to (p. 151).

THE PHOSPHORUS GROUP OF ELEMENTS.

THIS group is often represented as comprising nitrogen as well as phosphorus, arsenic, and the imperfect metals, vanadium, antimony, and bismuth. Nitrogen has already been described. So far as concerns the element nitrogen itself it will be seen that it has no resemblance to phosphorus and only a distant connection with it, arising chiefly out of the analogy between the compounds with hydrogen formed by these two elements.

Reserving antimony and bismuth for treatment at a later stage the characteristics of the group, fully exhibited by phosphorus and arsenic though only imperfectly so by antimony and bismuth, may be stated as follows:—The elements in question are solids, fusible and volatile, but less so in proportion as the atomic weight is greater. All are easily oxidisable when heated in the air and are readily attacked by chlorine. Their compounds with chlorine and with oxygen belong to two types represented respectively by the following general formulæ, in which E represents an atom of one of these elements,

$$\begin{array}{ll} ECl_3 & E_4O_6 \\ ECl_5 & E_4O_{10}. \end{array}$$

Their oxides united with the elements of water form powerful acids.

Phosphorus, arsenic, and antimony form compounds with hydrogen corresponding in composition, and to some extent in properties, with ammonia which is represented by the formula NH_3.

As in other groups of closely related elements, the atomic weights in the phosphorus group stand in the order of an arithmetical progression. The following is the most important series :—

	Atomic Weight.	Mean of Extremes.
Phosphorus, . . .	31	
Arsenic, ...	75	$\frac{120 + 31}{2} = 75{\cdot}5$.
Antimony, . . .	120	

PHOSPHORUS.

Symbol, P. Atomic weight, 31. Vapour-density, 62.

The name phosphorus (φῶς, light φέρω I bear), was formerly applied to any substance which emitted light spontaneously. It is, however, now given only to the element about to be described.

Phosphorus in the state of phosphate is contained in the ancient crystalline rocks and in lavas of modern origin. As these disintegrate

and crumble down into fertile soil, the phosphates pass into the organism of plants, and ultimately into the bodies of the animals to which the plants serve for food. The earthy phosphates play a very important part in the structure of the animal frame, by communicating stiffness and inflexibility to the bony skeleton.

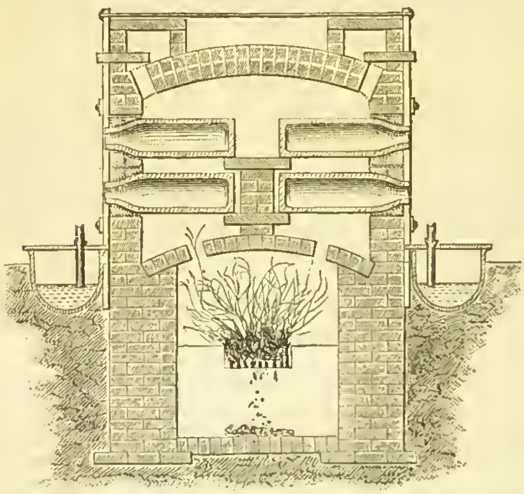
Phosphorus was discovered in 1669 by Brandt, of Hamburg, who prepared it from urine, by evaporating to a syrup and distilling the residue mixed with sand. It is now invariably prepared from a mineral phosphate, of which large deposits occur in Spain, Canada, the West Indies, and other countries.

The following is an outline of the method of preparation now adopted:—The phosphate of calcium (*apatite*) or of aluminium (*Redonda phosphate*) is ground to powder and mixed with diluted sulphuric acid in quantity sufficient to take out the whole of the metal in the form of sulphate and render the phosphorus soluble as phosphoric acid:—

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4.$$

The calcium phosphate is filtered off and the clear solution evaporated to a syrupy consistence and mixed with coal dust, and the drying completed at a high temperature in iron pans. In this process the coal is partly coked and the phosphoric acid is converted into metaphosphoric acid:— $H_3PO_4 = H_2O + HPO_3$.

Fig. 82.



The residue when quite dry is introduced into fireclay tube-shaped retorts which are arranged in a double row in a furnace by which they can be heated to bright redness, as shown in the adjoining figure.

The neck of each retort is closed by a wide bent tube terminating in an iron pipe which dips into a trough of water. Carbonic oxide and hydrogen escape accompanied by a little phosphoretted hydrogen and the vapour of phosphorus. The last condenses and collects under the surface of the water which protects it from the action of the air.

$$4HPO_3 + 12C = 2H_2 + 12CO + P_4.$$

The product is a reddish-brown fusible substance which is purified by melting and straining from a small quantity of an infusible oxide.

Phosphorus when pure is perfectly colourless but it usually presents the aspect of white wax, and is soft and flexible at common temperatures. It is usually sold in the form of sticks, which were formerly obtained by drawing up the melted substance into glass tubes. This dangerous process has, however, long been superseded by the plan of melting the phosphorus in a small tank by means of warm water, and allowing it to flow through brass tubes laid horizontally upon a table covered with water, from which the phosphorus may be drawn in the form of a continuous rod.

The density of solid phosphorus is 1·836 at 0°, and that of its vapour 4·35, air being unity, or 61·92 referred to hydrogen as unity. Applying the usual rule the molecular weight of phosphorus is therefore the double of this number or 124. Hence the formula must be written P_4, which represents a quantity equal to four times 31, which is the atomic weight.

Phosphorus melts at 44°, and boils at 280°. On slowly cooling melted phosphorus, well-formed dodecahedrons are sometimes obtained, but crystals are most easily formed by sealing up a piece of dry phosphorus in a large tube from which the air has been completely exhausted. The phosphorus slowly sublimes in brilliant crystals, resembling the diamond in form and lustre. Phosphorus is insoluble in water, and is usually kept immersed in that liquid, but it dissolves in oil, in mineral naphtha, and especially in carbon bisulphide. When set on fire in the air, it burns with a bright flame, generating phosphoric oxide. It is exceedingly inflammable, sometimes taking fire in the hand, and demands great care in its management; a blow or hard rub will very often kindle it. A stick of phosphorus held in the air always appears to emit a whitish smoke, which is luminous in the dark. This effect is chiefly due to a slow combustion which the phosphorus undergoes by the oxygen of the air, and upon it depends one of the methods employed for the analysis of air, as already described. It is singular that the slow oxidation of phosphorus may be entirely prevented by the presence of a small quantity of olefiant gas, or the vapour of ether, or some essential oil; phosphorus may even be distilled in an atmosphere containing vapour of oil of turpentine in considerable quantity. Neither does the action go on in pure oxygen—at least at the temperature of 15·5°, which is very remarkable; but if the gas be rarefied, or diluted with nitrogen, hydrogen, or carbon dioxide, oxidation is set up.

A very remarkable modification of this element is known by the name of red or, improperly, amorphous phosphorus. It was discovered by Schrötter, and is made by exposing common phosphorus for several days at a temperature of 240° to 250°, in an atmosphere which is unable to act chemically upon it. At this temperature it becomes red and opaque, and insoluble in carbon bisulphide, and is also unacted upon by alkaline solutions, whereby it may be separated from ordinary phosphorus.

It is manufactured by filling with common phosphorus a large

iron pot set in brickwork over a small fire grate. The mouth of the pot is closed, and heat applied, when, of course, the phosphorus melts, and ignites at the surface. The oxygen in the small confined portion of air is, however, immediately absorbed, and the heating can be continued without further loss of phosphorus. At the end of about a week the phosphorus becomes much less fusible and solidifies. The compact mass is extracted, ground to powder, and boiled with solution of soda, which extracts the unchanged waxy phosphorus, and leaves the new variety in the form of a dark red powder.

This substance is also formed when common phosphorus is melted in an atmosphere of nitrogen or carbon dioxide, in which it does not burn, and a very small quantity of iodine is thrown in. A good deal of heat is evolved, and the phosphorus is almost instantly converted into the red modification. This substance varies considerably in colour, according to the temperature at which it has been formed. Its density also varies from about 2·1 to 2·2. It is infusible, but when heated to a high temperature, about 350°, it is reconverted into the colourless kind. It does not fume in the air, neither is it luminous in the dark till the temperature is raised considerably. It may be preserved in contact with the air, and only after years shows signs of slow oxidation by the gradual accumulation of a mixture of phosphorous and phosphoric acids, in consequence of which it becomes damp.

Red phosphorus is largely consumed in the manufacture of matches, and especially as an ingredient in the coating applied to the boxes of safety matches.

Several other modifications of phosphorus are known, one of which appears as a white opaque crust on clear phosphorus when exposed to light. A crystalline variety of red phosphorus is obtainable by heating together common phosphorus and metallic lead, in a tube from which air is excluded, to a temperature above the melting point of lead. The mass, after cooling, is treated with dilute nitric acid, which dissolves out the lead, while the phosphorus remains in the form of nearly black rhombohedrons isomorphous with arsenic, antimony, and bismuth, and having the density 2·34.

Phosphorus Hydrides.

Phosphine.—*Phosphoretted Hydrogen*, PH_3.—This body is analogous in some of its chemical relations to ammonia gas ; its alkaline properties are, however, much weaker.

It may be obtained in a state of purity by heating phosphorous acid in a small retort, the acid being then resolved into phosphine and phosphoric acid :

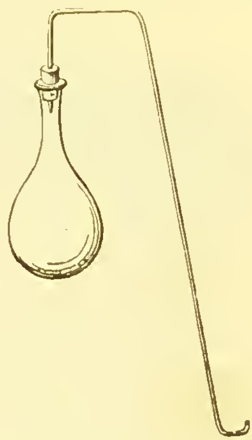
$$4H_3PO_3 = PH_3 + 3H_3PO_4 ;$$

or by heating phosphonium iodide with caustic potash :

$$PH_4I + KHO = PH_3 + KI + H_2O .$$

Thus obtained, the gas has a density of 1·20 (referred to air), or 16·98 (referred to hydrogen), which number is the half of its molecular weight. It contains three volumes of hydrogen and half a volume of phosphorus vapour, condensed into two volumes. It has a highly disagreeable odour of garlic, is slightly soluble in water, and burns with a brilliant white flame, forming water and phosphoric acid.

Fig. 83.



Experiment.—Phosphine may also be produced by boiling together, in a small flask, fitted with a tube of the form shown in the figure, solution of caustic potash and a few pieces of phosphorus as large as a pea ; the vessel should be filled to the neck, and the residual air displaced by coal gas to avoid risk of explosion. The extremity of the tube dips into water. On applying heat, the following reaction occurs :—

$$\underset{}{P_4} + \underset{\text{Potassium hydroxide.}}{3KHO} + 3H_2O = PH_3 + \underset{\text{Potassium hypophosphite.}}{3KPH_2O_2}$$

The phosphine prepared by this process has the singular property of spontaneous inflammability when admitted into the air or into oxygen gas ; the oxide smoke produces in a still atmosphere beautiful vortex rings. The experiment should be performed in a fume chamber. Reserve the solution for a future experiment. (*See* "Hypophosphorous Acid.")

Gas possessing the same property is obtained by the action of water upon calcium phosphide, a substance obtained in an impure state by igniting lime in phosphorus vapour. It is therefore used occasionally to produce a signal fire at sea.

When kept over water for some time, the gas loses the self-lighting property, without otherwise suffering appreciable change ; but if dried by calcium chloride, it may be kept unaltered for a much longer time. The spontaneous combustibility of the gas arises from the presence of the vapour of a liquid hydrogen phosphide, P_2H_4, which may be obtained in small quantity by conveying the gas produced by the action of water on calcium phosphide through a tube cooled by a freezing mixture. This substance forms a colourless liquid of high refractive power and very great volatility. It does not solidify at $-17·8°$ C. In contact with air it inflames instantly, and its vapour in very small quantity communicates spontaneous inflammability to pure phosphine, and to all other combustible gases. It is decomposed by light into gaseous phosphine, and a solid phosphide, P_4H_2, which is often seen on the inside of jars containing gas which, by exposure to light, has lost the property of spontaneous inflammation. Strong acids also cause the formation of this solid com-

pound, and consequently spontaneously inflammable gas loses this property after passing through strong hydrochloric acid. It is to be observed that pure phosphine gas itself becomes spontaneously inflammable if heated to the temperature of boiling water.

Phosphine decomposes several metallic solutions, giving rise to precipitates of insoluble phosphides.

Compounds of Phosphine with Hydracids.

Phosphine unites with hydrogen chloride, bromide, and iodide, forming crystalline compounds, which are in every respect analogons to the corresponding ammonium compounds (*q.v.*).

	Phosphonium.	Ammonium.
Chloride, . . .	PH_3HCl or PH_4Cl	NH_3HCl or NH_4Cl
Bromide, . . .	PH_3HBr or PH_4Br	NH_3HBr or NH_4Br
Iodide, ...	PH_3HI or PH_4I	NH_3HI or NH_4I.

The ammonium salts are quite stable at common temperatures and may be crystallised without change from water. The phosphonium componnds, on the contrary, are very unstable, the chloride and bromide being resolved at common temperatures into phosphine and the hydrogen chloride or bromide. The iodide is somewhat more stable, and may be preserved in a bottle, though in the air the crystals deliquesce, and are slowly decomposed.

The iodide is best prepared by the action of water upon a mixture of phosphorous iodide and phosphorus obtained by dissolving 10 parts of common phosphorus in carbon bisulphide, placing the solution in a retort with a wide neck, and adding gradually to it a solution of 17 parts of iodine in the same solvent. The carbon bisulphide is distilled off by a water bath, the last portion being expelled by a current of carbon dioxide. When the retort has become quite cold, water is allowed to drop slowly upon the residue, when much heat is generated, and the phosphonium iodide sublimes, and collects in the neck of the retort in the form of a white crystalline crust.

The reaction very complicated, but the final result is probably as follows:

$$3PI_3 + 10P + 24H_2O = 7PH_4I + 2HI + 6H_3PO_4.$$

Phosphorus Chlorides.

Phosphorus forms two chlorides, analogous in composition to the oxides, the quantities of chlorine combined with the same quantity of phosphorus being in the proportion of 3 to 5.

Phosphorus Trichloride, or Phosphorous Chloride, PCl_3, is prepared by passing a slow stream of dry chlorine over dry phosphorus contained in a flask or retort connected with a dry condenser.

The product is accompanied with a small quantity of the higher chloride, from which it must be freed by redistillation from some fresh phosphorus. Phosphorus trichloride is a thin, colourless liquid, which fumes in the air. It boils at 76°. Its density is 1·6. Thrown into water it sinks to the bottom, and is slowly decomposed, yielding phosphorous acid and hydrochloric acid: $PCl_3 + 3H_2O = 3HCl + H_3PO_3$.

Phosphorus Pentachloride, or **Phosphoric Chloride,** PCl_5, is formed when phosphorus is burned in excess of chlorine. As the product in this case is a solid substance, the flask or retort in which the phosphorus is placed must have a wide neck. A rapid stream of chlorine passed in causes the phosphorus to take fire, and burn with a pale flame. It may be also obtained by passing a stream of dry chlorine gas into the liquid trichloride, which becomes gradually converted into a solid crystalline mass. Phosphorus pentachloride is decomposed by water, yielding phosphoric and hydrochloric acids: $PCl_5 + 4H_2O = 5HCl + H_3PO_4$.

Phosphorus pentachloride, when vaporised, is resolved into the trichloride and free chlorine, the colour of which is visible.

Phosphorus Oxychloride, $POCl_3$, is produced, together with hydrochloric acid, when phosphorus pentachloride is heated with a quantity of water insufficient to convert it into phosphoric acid. It is best prepared by distilling the pentachloride with dehydrated oxalic acid or crystallised boric acid:

$$PCl_5 + H_2C_2O_4 = POCl_3 + 2HCl + CO_2 + CO$$
$$3PCl_5 + 2H_3BO_3 = 3POCl_3 + B_2O_3 + 6HCl.$$

It is a colourless liquid, of sp. gr. 1·7, having a very pungent odour, boiling at 107°, readily decomposed by water into hydrochloric and phosphoric acids.

A *thiochloride* of analogous composition is produced by the action of hydrogen sulphide on the pentachloride, or by direct addition of sulphur to the trichloride. It is a colourless mobile liquid, which boils at 125°, and is decomposed by water.

Phosphorus Iodides.

Two *iodides* are known, P_2I_4 and PI_3. Both are obtained by dissolving phosphorus and iodine in carbon bisulphide, mixing the solutions, and cooling the liquid till crystals are deposited. Whatever proportions of iodine and phosphorus may be used, these two compounds always crystallise out, mixed with excess either of iodine or of phosphorus. The *di-iodide* is an orange-red solid which melts at 110°, forming a red liquid. The *tri-iodide* melts at 55°, and crystallises on cooling in well-defined dark red prisms. Both are decomposed by water, yielding hydriodic and phosphorous acids, the di-iodide also depositing yellow flakes of phosphorus.

Phosphorus Fluorides, Etc.

Phosphorus Trifluoride, PF_3, is a colourless gas which is obtained by heating phosphorus tribromide with zinc fluoride and in other ways. It is incombustible, but may be made to combine with oxygen, forming phosphoryl fluoride, POF_3.

Phosphorus Pentafluoride, PF_5.—This interesting compound is obtained by the action of arsenic trifluoride on phosphorus pentachloride :

$$5AsF_3 + 3PCl_5 = 5AsCl_3 + 3PF_5,$$

or by adding bromine to phosphorus trifluoride. A bromo-fluoride, PF_3Br_2, is formed which spontaneously decomposes into phosphorus pentafluoride and pentabromide :

$$5PF_3Br_2 = 3PF_5 + 2PBr_5.$$

This is a colourless gas, having a density 63, compared with hydrogen. This corresponds to the formula PF_5, and since the gas is of great stability, the existence of this compound shows that phosphorus in combination with five atoms of a halogen may form a compound which is not dissociated or decomposed when converted into gas.

The pentachloride is resolved by heat into the trichloride and chlorine, and the pentabromide is similarly decomposed when converted into vapour.

The remaining halogen compounds of phosphorus are comparatively unimportant. A complete list of these compounds, as at present known, is given below.

...	PF_3	POF_3	PSF_3	PCl_2F_3	PF_5	...
...	...	...	...	PBr_2F_3	...	...
...	PCl_3	$POCl_3$	$PSCl_3$	...	PCl_5	...
...	...	$P_2O_3Cl_4$	...	...	...	...
...	PBr_3	$POBr_3$	$PSBr_3$	PBr_2Cl_3	PBr_5	PCl_3Br_4
...	...	$POBrCl_2$	$PSBrCl_2$	...	...	PCl_3Br_6
...	...	...	$P_2S_3Br_4$	...	...	...
...	...	...	PS_2Br	...	...	...
P_2I_4	PI_3	...	...	...	...	...

Phosphorus Oxides.

In addition to the unimportant insoluble monoxide, there are three definite oxides of phosphorus, in which the quantities of oxygen

united with the same quantity of phosphorus are to one another, as 3, 4, 5 :—

			Composition by weight.		
		Formula.	Phosphorus.		Oxygen.
Phosphorus Monoxide,	.	P_4O	124	+	116
Phosphorous Oxide,	.	P_4O_6	124	+	96
Phosphorus Tetroxide,	.	P_2O_4	62	+	64
Phosphoric Oxide,	.	P_4O_{10}	124	+	160

These three last oxides, unite with water and metallic oxides to form salts, called phosphites and phosphates, the hydrogen salts being also called phosphorous and phosphoric acid. There are also two other oxygen-acids of phosphorus, viz., hypophosphorous acid containing a smaller proportion of oxygen than phosphorous acid, and hypophosphoric acid intermediate in composition between phosphorous and phosphoric acids.

Phosphorus Monoxide, P_4O.—This is a red powder formed when phosphorus is burned in a limited supply of air, as for example by melting phosphorus under warm water and blowing air into it. It is insoluble in water, and therefore easily separated from the other oxides which are formed at the same time, and all of which dissolve in water giving an acid solution.

Hypophosphorous Acid, H_3PO_2.—When phosphorus is boiled with a solution of potash, lime, or baryta, water is decomposed, giving rise to phosphine and a hypophosphite : the first escapes as gas, and the hypophosphite remains in the solution :

$$2P_4 + 3BaH_2O_2 + 6H_2O = 3BaH_2(PO_2)_2 + 2H_3P.$$

The soluble hypophosphite may be crystallised out from the liquid by slow evaporation. On adding to the liquid the quantity of sulphuric acid necessary to precipitate the barium, the hypophosphorous acid is obtained in solution, and may be reduced to a syrupy consistence by evaporation. The pure acid is a white crystalline substance which melts at about 170°. The acid is very prone to absorb more oxygen, and is therefore a powerful deoxidising agent. Hypophosphites containing metals of the alkalis or alkaline earths, are soluble in water. Hypophosphorous acid reduces the heavy metals from solutions of their salts.

Experiment.—Take the solution obtained in the preparation of phosphine (p. 173), pour it off from any undissolved phosphorus, acidify slightly with dilute sulphuric acid, and add solution of copper sulphate. A dark brown precipitate of cuprous hydride, Cu_2H_2, is formed :

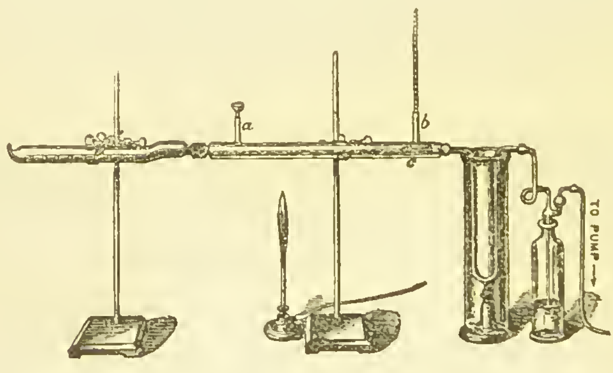
$$3H_3PO_2 + 4CuSO_4 + 6H_2O =$$
$$3H_3PO_4 + 2Cu_2H_2 + 4H_2SO_4.$$

Filter this off and warm it with some strong hydrochloric acid; hydrogen is evolved:

$$Cu_2H_2 + 2HCl = Cu_2Cl_2 + 2H_2.$$

Phosphorous Oxide, P_4O_6, is formed by the slow combustion of phosphorus in a stream of air. It is very fusible and somewhat volatile, and by taking advantage of this circumstance it may be separated without much difficulty from the higher oxide which is formed at the same time. Its formation may be easily demonstrated by burning a piece of phosphorus at one end of a piece of combustion tubing 5 or 6 feet long, through which a current of air is drawn. The snowy white deposit at the farther end of the tube will be found to melt on grasping the tube with the hand, or applying a gentle heat by any other means. It is most conveniently prepared in an apparatus devised by Thorpe and Tutton, who first obtained it in a pure state. A wide glass tube open at each end is connected at one extremity with a brass tube surrounded by a water-jacket, like a Liebig condenser. This in turn is attached to a U-shaped glass

Fig. 84.



tube, which can be surrounded by a freezing mixture, and which communicates below with a dry bottle for the reception of the product. If now phosphorus is introduced in successive portions into the open end of the wide glass tube, and made to burn by means of a stream of air drawn through the whole apparatus by an aspirator attached at the opposite extremity, the oxides formed are swept forward into the condenser. This part of the arrangement is kept at a temperature of about 25°, and the tube contains a loose plug of slag wool or asbestos, by means of which the phosphoric oxide is arrested, while the volatile phosphorous oxide passes on and is condensed in the U-tube. When a sufficient deposit of crystalline matter is observed in this tube, the freezing mixture is removed and the tube warmed gently. The crystalline oxide then melts and runs into the bottle.

Phosphorous oxide is a white solid which melts at 22·5°. It boils

at 173·1°. The density of its vapour corresponds with the formula P_4O_6, and not with the simpler expression P_2O_3. It oxidises on exposure to the air, and when dropped into warm oxygen gas it burns spontaneously with a vivid white light. Phosphorous oxide dissolves in cold water rather slowly, forming phosphorous acid :

$$P_4O_6 + 6H_2O = 4H_3PO_3.$$

Phosphorous Acid, H_3PO_3, is most conveniently prepared by adding water to the trichloride of phosphorus, when phosphorous acid and hydrochloric acid are produced :

$$PCl_3 + 3H_2O = 3HCl + H_3PO_3.$$

By evaporating the solution to the consistence of syrup, the hydrochloric acid is expelled, and the residue crystallises on cooling.

Phosphorous acid is very deliquescent, and very prone to attract oxygen and pass into phosphoric acid. When heated it is resolved into phosphoric acid and pure phosphine gas :

$$4H_3PO_3 = H_3P + 3H_3PO_4.$$

Experiment.—Into a large test-tube half filled with water drop a piece of phosphorus. Apply a gentle heat so as to melt the phosphorus, and then allow chlorine to pass, bubble by bubble, slowly into the phosphorus. The resulting solution contains both phosphorous and hydrochloric acids. To one portion of it add mercuric chloride ; a white precipitate of mercurous chloride is formed. To another portion add copper sulphate ; no precipitate is produced as with hypophosphorous acid.

Phosphorus Tetroxide, P_2O_4. When the product of the combustion of phosphorus in a limited supply of dry air is heated in a vacuum to about 290°, it is resolved into a residue of reddish suboxide and a sublimate of colourless crystals, which consist of the tetroxide. The new compound is very deliquescent and soluble in water, forming a mixture of phosphorous and phosphoric acids, the reaction corresponding to that of nitrogen tetroxide with water :

$$P_2O_4 + 3H_2O = H_3PO_3 + H_3PO_4.$$

Phosphoric Oxide, or *Phosphoric Anhydride,* P_4O_{10}.—When phosphorus is burned by the aid of a copious supply of dry air, snow-like phosphoric oxide is produced abundantly. Exposed to the air for a few moments, phosphoric oxide deliquesces to a liquid, and when thrown into water, combines with the latter with explosive violence, and is converted into metaphosphoric acid.

Experiment.—Place a small piece of phosphorus on a dry plate, ignite it and immediately cover with a large dry beaker or bell-jar. After the combustion is over, notice the red residue of amorphous phosphorus and the white flakes of oxide. The latter may be quickly collected by a dry spatula and dropped into water. A strongly acid

solution of metaphosphoric acid results; boil it for a quarter of an hour, then pour a little of it into a test-tube, add solution of silver nitrate and a few drops of solution of potash. A yellow precipitate of silver orthophosphate, Ag_3PO_4, is thrown down.

Phosphoric oxide prepared by combustion in air is, however, always contaminated with small quantities of the lower oxides of phosphorus. These may be detected by dissolving the product in water and adding to the solution a small quantity of mercuric chloride. On warming the liquid a white precipitate of mercurous chloride makes its appearance if phosphorous acid is present:

$$2HgCl_2 + H_2O + H_3PO_3 = Hg_2Cl_2 + 2HCl + H_3PO_4,$$

whereas no visible change occurs if the phosphoric acid is pure. To obtain pure phosphoric oxide the commercial substance must be heated in a combustion tube in a stream of dry oxygen gas, and the vapour carried through a mass of spongy platinum placed in the front part of the tube, heated to redness. The pure phosphoric oxide is then carried forward by the excess of oxygen, and may be collected in the form of a crystalline crust in a dry tube attached to the combustion tube.

Phosphoric oxide does not melt when heated, even in air compressed to upwards of seven atmospheres. It volatilises at a temperature below redness and is not altered by heat. Its vapour density at a bright red heat is 142 $(H=1)$ (Tilden and Barnett), whence the molecular weight is 284 and must be represented by the formula P_4O_{10}. This compound therefore conforms to the type of phosphorus itself and of the other oxides of phosphorus and the allied elements, arsenic and antimony, the volatilisable oxides of which have the formulæ As_4O_6 and Sb_4O_6 respectively.

Phosphoric Acid, *Common or Orthophosphoric Acid*, H_3PO_4.—This important compound may be obtained; (1) by dissolving phosphoric oxide in water and boiling the solution for some time; (2) by boiling phosphorus with diluted nitric acid till dissolved, and then evaporating off the excess of nitric acid; (3) by treating calcium phosphate in the form of bone-ash, with strong sulphuric acid sufficient to remove the greater part of the calcium in the form of calcium sulphate, dissolving out the soluble product with water and precipitating with a slight excess of ammonium carbonate, so as to get rid of the remainder of the calcium. The solution filtered from calcium carbonate then contains ammonium phosphate with a little sulphate. By evaporating this to dryness and heating the residual salt strongly, metaphosphoric acid remains and may be converted into common phosphoric acid by redissolving in boiling water.

Pure phosphoric acid may be obtained from the solution resulting from either of these operations by evaporating it at a low temperature to a thin syrup, and then exposing the liquid to further evaporation at common temperatures in a vacuum; phosphoric acid crystallises in rhombic prisms which melt at 41° – 42°.

Phosphoric acid forms three classes of salts by exchange of 1, 2, or 3 atoms of hydrogen for an equivalent quantity of a metal. The phosphates of sodium and of calcium for example are represented in the anhydrous state by the following formulæ :

$$\begin{array}{ll} NaH_2PO_4 & Ca(H_2PO_4)_2 \\ Na_2HPO_4 & Ca_2(HPO_4)_2 \\ Na_3PO_4 & Ca_3(PO_4)_2 \end{array}$$

When common phosphoric is exposed to heat it loses the elements of water and gives rise to two other acids : pyrophosphoric acid formed at about 215°, and metaphosphoric acid formed by heating common or pyrophosphoric acid to higher temperatures :

$$\begin{array}{lccccc} & 2H_3PO_4 & = & H_2O & + & \underset{\text{Pyro.}}{H_4P_2O_7} \\ & 2H_3PO_4 & = & 2H_2O & + & \underset{\text{Meta.}}{H_2P_2O_6} \\ \text{or} & H_4P_2O_7 & = & H_2O & + & \underset{\text{Meta.}}{H_2P_2O_6} \end{array}$$

These compounds are reconverted into common phosphoric acid by protracted boiling with water.

Pyrophosphoric Acid, $H_4P_2O_7$.—This is a solid glassy deliquescent substance soluble in water and slowly converted by boiling water into common phosphoric acid.

It forms four classes of salts, the composition of which is represented by the following formulæ in which M stands for one atom of a metal such as sodium :—

$$\begin{array}{l} MH_3P_2O_7 \\ M_2H_2P_2O_7 \\ M_3HP_2O_7 \\ M_4P_2O_7. \end{array}$$

Pyrophosphoric acid is distinguished from orthophosphoric acid by giving with silver nitrate a white precipitate.

Metaphosphoric Acid, $H_2P_2O_6$.—This compound resembles pyrophosphoric acid in its glassy aspect and general characters. It has no definite melting point, but generally liquefies when heated and at a red heat it boils and may be distilled, though with partial decomposition, being slowly resolved into water and phosphoric oxide so that the residue becomes gradually richer in that substance. The vapour density of metaphosphoric acid corresponds to the formula $H_2P_2O_6$ (Tilden and Barnett). This acid has usually been regarded as monobasic with the formula HPO_3, but the salts are rather complicated and several series are known which may be expressed by the general formula $(MPO_3)n$. They require further investigation.

Metaphosphoric acid is distinguished by giving a white precipitate

with silver nitrate, and by curdling albumen (white of egg). Pyro- and ortho-phosphoric acids do not coagulate albumen.

Hypophosphoric Acid, $H_4P_2O_6$.—This acid is one of the constituents of the acid liquid formed when phosphorus partially covered with water is exposed to the air, and may be separated as a sparingly soluble sodium salt by treating that liquid with carbonate or acetate of sodium. The pure acid is best prepared by decomposing its lead salt suspended in water with hydrogen sulphide. Its aqueous solution is strongly acid, and may be boiled without decomposition, but when evaporated to a syrup it is resolved by further heating into phosphorous and phosphoric acids. It gives a white precipitate with silver salts, and is oxidised by potassium permanganate to phosphoric acid. It is quadribasic, yielding, for example, the sodium salts :

$$Na_4P_2O_6, \qquad Na_3HP_2O_6, \qquad Na_2H_2P_2O_6.$$

Phosphorus with Sulphur.

Sulphides.—When ordinary phosphorus and sulphur are heated together in the dry state, or melted together under water, combination takes place, attended with vivid combustion and sometimes with violent explosion. When amorphous phosphorus is used, the reaction is not explosive, though still very violent.

The following compounds of sulphur and phosphorus have been prepared :—

	Composition by weight.		
	Phosphorus.		Sulphur.
Monosulphide, P_4S,	124	+	32
Sesquisulphide, P_4S_3,	124	+	96
Phosphorous sulphide, P_4S_6,	124	+	192
Phosphoric sulphide, P_2S_5 or P_4S_{10},	124	+	320

The third and fourth are analogous to phosphorous and phosphoric oxides respectively. The compounds may all be formed by heating the two solids together in the required proportions.

Phosphoric sulphide, which is the most important member of the series, may also be obtained by dissolving phosphorus and sulphur separately in carbon bisulphide and then heating the solution in a sealed tube to a temperature above 200°. It forms yellow volatile crystals.

All these compounds are soluble in caustic alkali, and they also unite with metallic sulphides, forming thio-compounds, which may be regarded as phosphites or phosphates, in which oxygen is more or less replaced by sulphur. For example :

Sodium monothiophosphate,	Na_3PSO_3
Sodium dithiophosphate,	$Na_3PS_2O_2$
Copper thiometaphosphate,	CuP_2S_6.

Phosphorus and Nitrogen.

Phospham, PN_2H, probably $PN(NH)$ or $P_3N_3(NH)_3$, formed by passing dry ammonia over PCl_5 and heating the product out of contact with the air as long as sal-ammoniac sublimes, is a light white powder insoluble in water and infusible at a red heat. When heated in the air, it slowly oxidises, giving off white fumes; and when moistened and heated it yields ammonia and metaphosphoric acid: $PN_2H + 3H_2O = 2NH_3 + PO_3H$. By fusion with caustic alkali, it is decomposed, with evolution of light and heat, yielding ammonia and an orthophosphate: $PN_2H + 3KOH + H_2O = 2NH_3 + PO(OK)_3$.

Phosphoryl Triamide, $PO(NH_2)_3$, the amide of orthophosphoric acid, is obtained by the action of ammonia on phosphorus oxychloride: $POCl_3 + 6NH_3 = 3NH_4Cl + PO(NH_2)_3$. On dissolving out the sal-ammoniac by water, the triamide remains as a white amorphous powder, not acted upon by boiling with water or aqueous potash-solution, but decomposed by sulphuric acid into phosphoric acid and ammonia: $2PO(NH_2)_3 + 3H_2SO_4 + 6H_2O = 2PO(OH)_3 + 3(NH_4)_2SO_4$. By fusion with potash it yields ammonia and potassium phosphate.

Phosphoryl Imido-amide, $PO(NH)(NH_2)$, is obtained, together with sal-ammoniac, by the action of ammonia on phosphorus penta-chloride. It is insoluble in water, and is slowly converted by boiling with water into acid ammonium phosphate: $PO(NH)(NH_2) + 3H_2O = PO(OH)(ONH_4)_2$.

Thiophosphoryl Triamide, $PS(NH_2)_3$, is formed, together with sal-ammoniac, by the action of ammonia on phosphorus thiochloride. It is a white amorphous mass, decomposing when heated, and converted by hot water into ammonium thiophosphate, $PS(ONH_4)_3$.

Phosphoryl Nitride, PON, obtained by heating phosphamide or phosphoryl triamide out of contact with the air, is a white amorphous powder, which melts at a red heat and resolidifies to a vitreous mass. It is not attacked by nitric acid, but is converted by fusion with potash into ammonia and potassium orthophosphate: $PON + 3KOH = NH_3 + PO(OK)_3$.

Pyrophosphotriamic Acid, $P_2O_3(OH)(NH_2)_3$.—This compound, derived from pyrophosphoric acid, $P_2O_3(OH)_4$, by substitution of $3NH_2$ for 3HO, is obtained by passing ammonia into phosphorus oxychloride without cooling, and boiling the product with water, $2POCl_3 + 9NH_3 + 2H_2O = 6NH_4Cl + P_2O_3(OH)(NH_2)_3$. It is an amorphous tasteless powder, decomposed by boiling with water into ammonia and *pyrophosphodiamic acid*, $P_2O_3(OH)_2(NH_2)_2$, which is an amorphous mass soluble in water and decomposed by heat into ammonia and phosphoric oxide: $P_2O_3(OH)_2(NH_2)_2 = 2NH_3 + P_2O_5$. By continued boiling with water it is converted into pyro-

phosphamic acid, $P_2O_3(OH)_3NH_2$, which, when similarly treated, yields ammonium phosphate and pyrophosphoric acid: $P_2O_3(OH)_3NH_2 + HOH = NH_3 + P_2O_3(OH)_4$.

Nitrogen Chlorophosphide, $P_3N_3Cl_6$, is formed by distilling the product of the action of ammonia on phosphorus pentachloride, or by distilling 1 part of the pentachloride with 2 parts sal-ammoniac. It sublimes in thin transparent six-sided plates melting at 110° and boiling at 240°. It is insoluble in water, but is slowly decomposed thereby, with formation of pyrophosphodiamic acid: $2P_3N_3Cl_6 + 15H_2O = 12HCl + 3P_2O_3(OH)_2(NH_2)_2$.

ARSENIC.

Symbol, As. Atomic weight, 75. Vapour-density, 150.

Arsenic is sometimes found native; but it occurs chiefly as a constituent of many minerals, combined with sulphur, and with metals. Its two sulphides, As_2S_2 and As_2S_3, have long been known as natural minerals, the former under the name *realgar*, or *ruby sulphur*, the latter as *orpiment*, a corruption of the Latin *auri pigmentum*. In the oxidised state, it has been found in very minute quantity in some mineral waters. The largest proportion is derived from the roasting of natural arsenides of iron, nickel, and cobalt. The operation is conducted in a reverberatory furnace, and the volatile products are condensed in a long and nearly horizontal chimney, or in a kind of tower of brickwork, divided into numerous chambers. The crude arsenious oxide thus produced is purified by sublimation, and is then heated with charcoal in a retort; the arsenic is reduced, and readily sublimes.

Arsenic has a steel-grey colour, and metallic lustre: It is crystalline and very brittle; it tarnishes in the air, but may be preserved unchanged in pure water. Its density, in the solid state, is 5·7 to 5·9. When heated, it volatilises without fusion, and if air be present, oxidises to arsenious oxide. Its vapour-density, compared with that of hydrogen, is 149·8, which is twice its atomic weight, so that its molecule in the gaseous state, like that of phosphorus, contains twice as many atoms as a molecule of hydrogen, and is therefore represented by the formula As_4. The vapour has the odour of garlic.

Arsenic combines with metals in the same manner as sulphur and phosphorus, which latter it resembles in many respects.

Arsenic, like phosphorus, unites with oxygen in two proportions, but it is not capable of uniting with more than three atoms of any one monad element. Thus it forms the compounds AsH_3, $AsCl_3$, $AsBr_3$, etc., but no compound corresponding to the pentachloride of phosphorus or of antimony. A pentafluoride is, however, known to

exist in combination with other fluorides. But just as ammonia, NH_3, can take up the elements of hydrogen chloride to form sal-ammoniac, NH_4Cl, so likewise can arsenetted hydrogen or arsine, AsH_3, unite with the chlorides, bromides, etc., of the groups, methyl, ethyl, etc., to form compounds such as the following :

Arsenmethylium chlorine, .	$AsH_3(CH_3)Cl$.
Arsenethylium bromide, . .	$AsH_3(C_2H_5)Br$.

The two oxides, viz., arsenious oxide, As_4O_6, and arsenic oxide, As_4O_{10}, produce acids and salts corresponding to the phosphorous and phosphoric compounds : the arsenates, in particular, are isomorphous with the orthophosphates, and resemble them closely in many respects.

Hydrides.—*Arsine* or *Arsenetted hydrogen*, AsH_3, analogous in composition to ammonia and phosphine, is obtained pure by the action of strong hydrochloric acid on an alloy of equal parts of zinc and arsenic, and is produced in greater or lesser proportion whenever hydrogen is set free in contact with arsenious acid. Arsenetted hydrogen is a colourless gas, of density 2·695 (air = 1) or 38·9 (hydrogen = 1), slightly soluble in water, and having the smell of garlic. It burns, when kindled, with a blue flame, generating arsenious acid. It is also decomposed into hydrogen and arsenic by transmission through a red-hot tube. Many metallic solutions are precipitated by this substance. When inhaled, it is exceedingly poisonous even in very minute quantity.

The solid *hydride*, As_2H_4 or As_4H_2, is produced by passing an electric current through water, the negative pole being formed of metallic arsenic ; also when potassium or sodium arsenide is dissolved in water. It is a brown powder, which gives off hydrogen when heated in a close vessel, and burns when heated in the air.

Arsenious Chloride, $AsCl_3$.—This, the only known chloride of arsenic, is produced, with emission of heat and light, when powdered arsenic is thrown into chlorine gas. It is prepared by distilling a mixture of 1 part of metallic arsenic and 6 parts of corrosive sublimate, and by distilling arsenious oxide with strong hydrochloric acid, or with a mixture of common salt and sulphuric acid. It is a colourless, volatile liquid, which boils at 130°, and is decomposed by water into arsenious and hydrochloric acids.

Arsenious Bromide, $AsBr_3$, prepared by adding powdered arsenic to a solution of bromine in carbon sulphide, forms colourless transparent crystals having a strong arsenical odour, a density 3·66, melting at 20°, and boiling at 220°. It is decomposed by water like the chloride.

Arsenious Diiodide, AsI_2 or As_2I_4, is a dark red crystalline compound, formed by heating arsenic and iodine together in proper proportions.

Arsenious Iodide, AsI_3, prepared in like manner, or by passing gaseous hydrogen iodide into arsenious chloride, crystallises in bright red hexagonal plates having a density 4·39.

Arsenic Pentiodide, AsI_5, is said to be produced by heating the triiodide with more iodine.

Arsenious Fluoride, AsF_3, prepared by distilling a mixture of 4 parts of arsenious oxide and 5 parts of fluorspar with 10 parts of strong sulphuric acid, is a limpid liquid boiling at 63°, and having a density 2·73. It has a strong pungent odour, fumes in the air, and produces serious wounds on the skin. It attacks glass, and is decomposed by water into arsenious and hydrofluoric acids. It dissolves in aqueous ammonia, and forms a crystalline compound with the gas. The *pentafluoride* is not known in the free state, but the compound AsF_5,KF is obtained in colourless crystals by dissolving potassium arsenate in hydrofluoric acid.

Arsenious Oxide, As_4O_6, also called *white arsenic*, is produced in the manner already mentioned. The density of the vapour points to the formula As_4O_6 for its molecule. It is commonly met with in the form of a heavy, white, glassy-looking substance, with smooth conchoïdal fracture, as though it had undergone fusion. When freshly prepared it is often transparent, but becomes opaque by keeping, at the same time slightly diminishing in density, and acquiring a greater degree of solubility in water. Vitreous white arsenic has the specific gravity 3·682, while the opaque crystalline variety has the specific gravity 3·646. 100 parts of water at 100° dissolve about 11·5 parts of the opaque variety; the larger portion separates, however, on cooling, leaving about 3 parts dissolved: the solution, which contains *arsenious acid*, H_3AsO_3, feebly reddens litmus. Cold water, agitated with powdered arsenious oxide, takes up a still smaller quantity. It is much more soluble in hydrochloric acid, and separates from the solution in large crystals, the deposition of which in the dark is attended with a bright and continuous luminosity. It also occurs naturally crystallised, sometimes in octahedrons, sometimes in tetrahedrons.

Alkalis dissolve arsenious oxide freely, forming arsenates; compounds with baryta, strontia, lime, magnesia, and other metallic oxides, have also been formed. The arsenites are, however, very unstable. Those which have the composition M_3AsO_3, are regarded as normal salts; there are also arsenites containing $M_4As_2O_5$, and $MAsO_2$, beside acid salts. The most important of the arsenites are tripotassium arsenite, K_3AsO_3, which is used in medicine in the preparation known as Fowler's solution, or *liquor arsenicalis*; Scheele's green, $CuHAsO_3$, a brilliant pigment; Schweinfurth green, a compound of arsenite and acetate, $3Cu(AsO_2)_2.Cu(C_2H_3O_2)_2$; and the silver salt, Ag_3AsO_3, a substance often obtained as a yellow precipitate in testing for arsenic.

The oxide has a slightly sweetish and astringent taste, and is a most fearful poison.

Arsenic Oxide and Arsenic Acid.—When powdered arsenious oxide is dissolved in hot hydrochloric acid, and oxidised by the addition of nitric acid, the latter being added as long as red vapours are produced, the whole then cautiously evaporated to complete dryness, and the residue heated to low redness, arsenic oxide remains in the form of a white deliquescent mass. When strongly heated, it is resolved into arsenious oxide and free oxygen. As it is not volatile without decomposition, its vapour density has never been ascertained. Consequently the formula for the molecule of this compound is uncertain, but since it has been ascertained that the highest oxide of phosphorus is P_4O_{10}, it may be inferred by analogy that the arsenic oxide is As_4O_{10}.

In water it dissolves slowly but completely, giving a highly acid solution, which, on being evaporated to a syrupy consistence, deposits, after a time, hydrated crystals of arsenic acid, containing $2H_3AsO_4,H_2O$. These crystals, when heated to 100°, give off their water of crystallisation and leave *orthoarsenic acid*, H_3AsO_4; at 140°–160° *pyroarsenic acid*, $H_4As_2O_7$, corresponding to pyrophosphoric acid, is left; and at 260° *metarsenic acid*, $HAsO_3$, corresponding to metaphosphoric acid. The aqueous solutions of the three hydrates and of the anhydrous oxide exhibit exactly the same characters, and all contain trihydric arsenate, the other hydrates being immediately converted into that compound when dissolved in water; in this respect the hydrates of arsenic oxide differ essentially from those of phosphoric oxide.

Arsenic acid is a tribasic acid, forming salts isomorphous with the corresponding phosphates. An arsenate is formed when a mixture of arsenious oxide with nitrate of potassium or sodium is thrown into a red-hot crucible. The mass melts and effervesces from escape of oxides of nitrogen, and on cooling is easily soluble in water. A *sodium arsenate*, $Na_2HAsO_4,12H_2O$, undistinguishable in appearance from common sodium phosphate, may be prepared in this manner, or by adding the carbonate to a solution of arsenic acid, until an alkaline reaction is apparent, and then evaporating. This salt also crystallises with 7 molecules of water. Another arsenate, $Na_3AsO_4,12H_2O$, is produced when sodium carbonate in excess is fused with arsenic acid, or when the preceding salt is mixed with caustic soda. A third, NaH_2AsO_4,H_2O, is made by substituting an excess of arsenic acid for the solution of alkali. The alkaline arsenates which contain basic hydrogen lose the latter in the form of water at a red heat, but, unlike the phosphates, recover it when again dissolved. The arsenates of the alkalis are soluble in water; those of the earths and other metallic oxides are insoluble, but are dissolved by acids. The reddish-brown precipitate of silver arsenate, Ag_3AsO_4, with silver nitrate is highly characteristic of arsenic acid.

Sulphides.—*Arsenious disulphide*, As_2S_2, occurs native as *Realgar*. It is formed artificially by heating arsenic acid with the proper proportion of sulphur. It is an orange-red, fusible, and volatile substance, employed in painting, and by the pyrotechnist in making *white fire*.

Arsenious trisulphide, or *arsenious sulphide*, As_2S_3 (or As_4S_6?), also occurs native as *Orpiment*, and is prepared artificially by fusing arsenic with the appropriate quantity of sulphur, or by precipitating a solution of arsenious acid with hydrogen sulphide. It is a golden-yellow, crystalline substance, fusible, and volatile by heat. A cold solution of arsenic acid is not immediately precipitated by hydrogen sulphide, but after some hours the solution, saturated with hydrogen sulphide, yields a light yellow deposit of sulphur, the arsenic acid being reduced to arsenious acid, which is then gradually converted into lemon-yellow arsenious sulphide. In boiling solutions the precipitation takes place immediately. The mixture of sulphur and trisulphide thus produced was formerly regarded as a pentasulphide analogous to arsenic oxide.

Arsenic sulphide, As_2S_5 (or As_4S_{10}?), is a yellow, fusible substance obtained as a precipitate by the addition of an acid to a solution of a thioarsenate:

$$2K_3AsS_3 + 6HCl = 6KCl + 2H_3AsS_3,$$

and

$$2H_3AsS_3 = 3H_2S + As_2S_5.$$

The sulphides of arsenic are thioanhydrides, which are capable of uniting with other metallic sulphides to form sulphur salts. Those of the disulphide are called hypothioarsenites; they are but little known. The salts of arsenious sulphide are called thioarsenites. Their composition may be represented by that of the potassium salts, viz., $KAsS_2$, $K_4As_2S_5$, and K_3AsS_3. Of these the second class are the most common. The thioarsenites of the alkali metals and alkaline earth-metals are soluble in water, and may be prepared by digesting arsenious sulphide in the solutions of the corresponding hydrates or sulphydrates; the rest are insoluble, and are obtained by precipitation. Thioarsenates, analogous in composition to the arsenates, are produced, in like manner, by digesting a mixture of sulphur and arsenious sulphide in solutions of alkaline hydrates or sulphydrates; also by passing gaseous hydrogen sulphide through solutions of arsenates. There are three thioarsenates of potassium, containing $KAsS_3$, $K_4As_2S_7$, and K_3AsS_4, which correspond respectively to meta-, pyro-, and ortho-arsenates. The thioarsenates of the alkali-metals and alkaline earth-metals are soluble in water; the rest are insoluble, and are obtained by precipitation.

Detection of Arsenic in cases of Poisoning.

Arsenious acid is distinguished by characters which cannot be mistaken. Its high density and slight solubility in water cause it to

collect in the heavier parts of any deposit from a watery liquid, while its volatility enables it to be separated easily from the majority of common mineral substances. The crystalline form of the sublimate thus obtainable is also highly characteristic, and easily recognised under the microscope.

Silver nitrate, mixed with a solution of arsenious acid in water, occasions no precipitate, or merely a faint cloud; but if a little alkali be added, a yellow precipitate of silver arsenite immediately falls. This precipitate is exceedingly soluble in excess of ammonia, which must therefore be added with great caution; it is likewise very soluble in nitric acid.

Cupric sulphate gives no precipitate with solution of arsenious acid, until a little alkali has been added, when a brilliant green precipitate (Scheele's green) falls, which also is very soluble in excess of ammonia.

Hydrogen sulphide, passed into a solution of arsenious acid, to which a few drops of hydrochloric or sulphuric acid have been added, throws down a copious bright yellow precipitate of orpiment, which is easily dissolved by ammonia, and reprecipitated by acids.

Fig. 85.

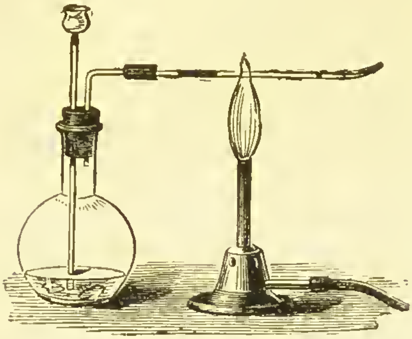
Solid arsenious oxide, heated in a narrow glass tube with small fragments of dry charcoal (fig. 85, *b*), affords a sublimate of metallic arsenic in the shape of a brilliant steel-grey metallic ring, *a*. A portion of this heated in a second glass tube, with access of air, yields, in its turn, a sublimate of colourless, transparent, octahedral crystals of arsenious oxide.

All these experiments, which *jointly* give demonstrative proof of the presence of the substance in question, may be performed with perfect precision and certainty upon exceedingly small quantities of material.

The detection of arsenious acid in complex mixtures, containing organic matter and common salt, as beer, gruel, soup, etc., or the fluid contents of the stomach in cases of poisoning, is more difficult. Such organic mixtures refuse to filter, or filter very slowly. The following plan is usually successful in producing a liquid from which the organic matters can be removed by filtration: Oil of vitriol, itself perfectly free from arsenic, is mixed with the suspected liquid, in the proportion of about a measured ounce to a pint, and the whole is boiled in a flask for half an hour, or until a complete separation of solid and liquid matter becomes manifest. The liquid is then filtered, and through a portion of the filtered solution, when cold, a current of hydrogen sulphide is passed, and the liquid is warmed, to facilitate the deposition of the arsenious sulphide, which falls in combination with organic matter, which often communicates to it a dirty colour. Another portion of the suspected liquid may be sub-

mitted to Marsh's test. A flask, fitted as in figure 86, is charged with pure granulated zinc, and dilute sulphuric acid added till hydrogen is freely evolved. A little of the liquid is added, the escaping gas is burned at a jet, and a piece of porcelain held in the flame, when any admixture of arsenetted hydrogen is at once known by the production of a brilliant black metallic spot of reduced arsenic on the porcelain ; or the gas is passed through a glass tube heated at one or two places to redness, whereby the arsenetted hydrogen is decomposed, a ring of metallic arsenic appearing beyond the heated portion of the tube.

Fig. 86.



Antimonetted hydrogen, however, gives a similar result. In order to distinguish the two substances, the deposit may be tested by adding a drop of solution of chlorinated lime, which dissolves the arsenic but not the antimony, or the gas may be passed into a solution of silver nitrate. Both gases give rise to a black precipitate, which, in the case of antimonetted hydrogen, consists of silver antimonide, Ag_3Sb :

$$SbH_3 + 3AgNO_3 = SbH_3 + 3HNO_3,$$

while, in the case of arsenetted hydrogen, it is pure silver, the arsenic being then converted into arsenious acid :

$$AsH_3 + 6AgNO_3 + 3H_2O = 6Ag + H_3AsO_3 + 6HNO_3.$$

Silver arsenite remains dissolved in the nitric acid which is liberated by the precipitation of the silver, and may be thrown down with its characteristic yellow colour by cautiously adding dilute ammonia to the liquid filtered off from the black precipitate. The black silver antimonide, when carefully washed, and subsequently boiled with a solution of tartaric acid, yields a solution containing antimony only, from which hydrogen sulphide separates the characteristic orange-yellow precipitate of antimonious sulphide.

A slip of copper-foil boiled in the poisoned liquid, previously acidulated with hydrochloric acid, withdraws the arsenic, and becomes covered with a white alloy. By heating the metal in a glass tube the arsenic is expelled, and oxidised to arsenious acid. This is called Reinsch's test.

CARBON.

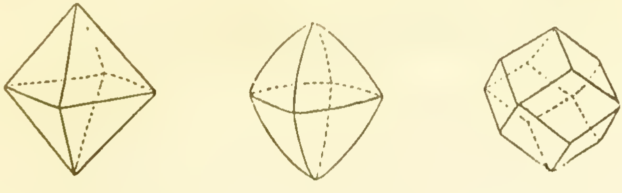
Symbol, C. Atomic weight, 12.

This element occurs in a state of purity, and crystallised, in two distinct and very dissimilar forms—namely, as diamond, and as graphite or plumbago. It constitutes a large proportion of all organic structures, animal and vegetable: when these latter are exposed to destructive distillation in close vessels, a great part of their carbon remains, obstinately retaining some of the hydrogen and oxygen, and associated with the earthy and alkaline matter of the tissue, giving rise to the many varieties of charcoal, coke, etc. This residue, when perfectly separated from foreign matter, constitutes a third variety of carbon.

The most abundant store of carbon is found in the carbonates of calcium and magnesium, which exist in such large quantities in the earth's crust, and in the several varieties of limestone constitute the material of which entire mountain ranges are composed. Carbon dioxide also exists as a component of the atmosphere.

1. The *diamond* is one of the most remarkable substances known: long prized on account of its brilliancy as an ornamental gem, the discovery of its curious chemical nature confers upon it a high degree of scientific interest. Several localities in India, the Island of Borneo, South Africa, and Brazil, furnish this beautiful substance. It is always distinctly crystallised, often quite transparent and colourless, but now and then having a shade of yellow, pink, or blue. The origin and true geological position of the diamond are unknown; it is always found imbedded in gravel and transported materials whose history cannot be traced. The crystalline form of the diamond is that of the regular octahedron or cube, or some figure geometrically connected with these. Many of the octahedral crystals exhibit a very peculiar appearance, arising from the faces being curved or rounded, which gives to the crystal an almost spherical figure. (*See* also Crystalline Forms; Cubic System.)

Fig. 87.



The specific gravity of diamond varies from about 3·3 to 3·5. It does not conduct electricity.

Carbon is known to dissolve in molten iron, from which it partly separates on cooling in the form of graphite. It has lately been discovered by Moissan that, if the temperature of the iron is raised

to a very high degree by heating in an electric furnace, and the metal is then cooled rapidly by plunging it into melted lead, the carbon which separates from the interior portions takes the form of diamond of various degrees of purity. This difference appears to be the effect of the enormous pressure exercised by the external crust which first solidifies upon the still fluid portions of metal within during the process of crystallisation.

The diamond is the hardest substance known : it admits of being split or cloven without difficulty in particular directions, but can only be cut or abraded by a second portion of the same material; the powder rubbed off in this process serves for polishing the new faces, and is also highly useful to the lapidary and seal-engraver. One curious and useful application of the diamond is made by the glazier; a *fragment* of this mineral, like a bit of flint, or any other hard substance, scratches the surface of glass; a *crystal* of diamond, having the rounded octahedral figure spoken of, held in one particular position on the glass—namely, with an edge formed by the meeting of two adjacent faces—presented to the surface and then drawn along with gentle pressure, causes a split or cut, which penetrates to a considerable depth into the glass, and determines its fracture with perfect certainty. Though hard, the diamond is somewhat brittle, and is easily broken by a blow, the fragments exhibiting conchoidal fracture.

The diamond is infusible and unalterable even by a very intense heat, provided air be excluded; but when heated, thus protected, in the electric arc, it is converted into coke or graphite; heated strongly in oxygen, it burns without flame, yielding carbon dioxide gas.

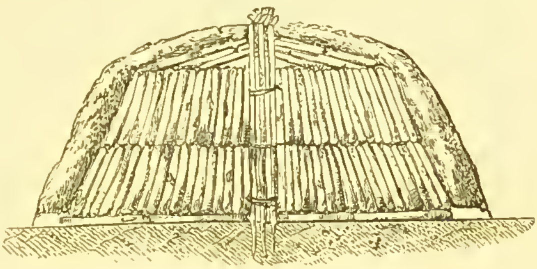
2. *Graphite* appears to consist essentially of pure carbon, although most specimens contain iron, the quantity of which varies from a mere trace up to 5 per cent. Graphite is a somewhat rare mineral; the finest and most valuable for the manufacture of so-called "black lead" pencils was formerly obtained from Borrowdale, in Cumberland, where a kind of irregular vein is found traversing the ancient slate beds of that district, but the mine is now nearly exhausted. Large quantities of graphite are imported from Germany, the East Indies, and the United States.* Crystals are not common; when they occur, they have the figure of a short six-sided prism—a form bearing no geometric relation to that of the diamond.

* The graphite which can be directly cut for pencils occurring only in limited quantity, powdered graphite, obtained from the inferior varieties of the mineral, is usually consolidated by pressure for this purpose. A chemical process for the mechanical division of graphite was suggested by the late Sir Benjamin Brodie, which consists in introducing the coarsely powdered graphite, previously mixed with $\frac{1}{14}$ of its weight of potassium chlorate, into 2 parts of concentrated sulphuric acid, which is heated in a water-bath until the evolution of acid fumes ceases. The acid is then removed by water, and the graphite dried. Thus prepared, this substance, when heated to a temperature approaching a red heat, swells up to a bulky mass of finely divided graphite. This process is too expensive for general use.

Graphite is often formed artificially in certain metallurgic operations; the brilliant scales which separate from some varieties of melted cast-iron on cooling, called by the workmen "kish," consist of graphite.

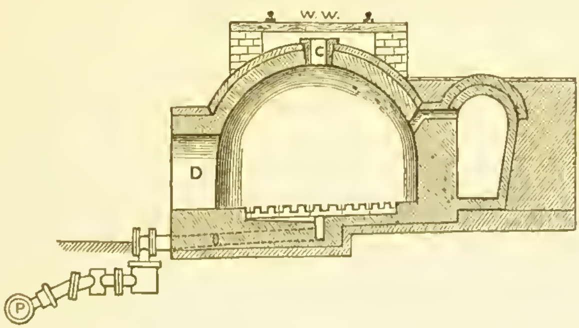
3. *Amorphous Carbon.*—Lamp-black, the soot produced by the imperfect combustion of oil or resin, is the best example that can be given of carbon in its uncrystallised state. To the same class belong the different kinds of charcoal. That prepared from wood, either by distillation in an iron retort, or by the smothered combustion of a pile of faggots partially covered with earth, as shown in the accompanying figure 88, is the most valuable as fuel. Coke, the charcoal of pit-coal, contains a large quantity of earthy matter, and some sulphur, the quality depending very much upon the mode of preparation.

Fig. 88.



Coke is sometimes made by partial combustion of coal in heaps or *piles* similar in form to the charcoal pile, but the best qualities of hard coke are obtained by carrying on the same operation in ovens, of which one form is represented in section in the accompanying figure 89. C is the charging door through which the coal is introduced from the waggon-way above. D is the door by which the coke

Fig. 89.



is raked out; and P is a section of the pipe by which, in this form of apparatus, the gases and vapours are drawn away from the heated coal. The combustion proceeds from above downwards.

Charcoal from bones and animal matters in general is a very valuable substance, on account of the extraordinary power it possesses of removing colouring matters from organic solutions; it is used for

this purpose by the sugar-refiner to a very great extent, and also by the manufacturing and scientific chemist. The property in question is possessed also in a small degree by all kinds of charcoal.

Charcoal made from box, or other dense wood, has especially the property of condensing gases and vapours into its pores; of ammoniacal gas it is said to absorb not less than ninety times its volume, while of hydrogen it takes up less than twice its own bulk, the quantity being apparently connected with the capacity of the gas for liquefaction. This property of absorbing gases, as well as the decolorising power, no doubt depends in some way upon the same peculiar action of surface so remarkable in the case of platinum in a mixture of oxygen and hydrogen. The absorbing power is, indeed, considerably increased by saturating charcoal with solution of platinum, and subsequently igniting it, so as to coat the charcoal with a thin film of platinum. Stenhouse, who suggested this plan, found that the gases thus absorbed undergo a kind of oxidation within the pores of the charcoal.

Carbon and Hydrogen.

The compounds of these elements are exceedingly numerous, and their complete study, together with that of their compounds and substitution-derivatives, constitutes a special branch of chemical science, usually called "Organic Chemistry," because the majority of them were originally obtained only by the decomposition of more complex bodies of organic origin. Many of them are, however, now obtainable by processes of purely chemical character without the use of materials derived from animal or vegetable sources. The following are a few of the more important compounds of carbon and hydrogen.

Acetylene, or *Ethine*, C_2H_2.—This is a colourless gas producible in small quantity by direct union of carbon with hydrogen by passing a stream of hydrogen gas through a globe in which the electric arc is maintained between carbon poles. The same compound is formed when coal gas, marsh gas, ether vapour, or other carbon compound is burned with an insufficient amount of air. It may be recognised by its disagreeable odour when a Bunsen burner becomes ignited inside the tube. The acetylene in either case may be separated from the other gases present by taking advantage of the property it possesses of forming a peculiar compound containing copper when brought into contact with an ammoniacal solution of cuprous chloride. A red precipitate is then formed from which pure acetylene may be obtained by filtering it off and mixing it with strong hydrochloric acid. There is some doubt as to the composition of this compound which may be represented either as containing the carbon of acetylene with copper in place of hydrogen, or as containing acetylene united to cuprous oxide. The action of

hydrogen chloride may then be expressed by one of the following equations :

$$C_2Cu_2 + 2HCl = C_2H_2 + Cu_2Cl_2$$

or

$$C_2H_2Cu_2O + 2HCl = C_2H_2 + Cu_2Cl_2 + H_2O.$$

Acetylene may be made more readily and abundantly by the action of water upon calcium carbide, a compound now manufactured in quantity by heating in an electric furnace a mixture of lime and carbon :

$$Ca_2C_2 + 2H_2O = 2Ca(HO)_2 + C_2H_2.$$

Acetylene burns at the end of a tube with a smoky flame, but when diluted with hydrogen or some other combustible gas, or when burned in a pure state at a suitable burner it gives a flame possessing great luminosity. On this account it is proposed to manufacture it on a large scale for the purpose of adding to the illuminating power of common coal gas.

Methane or Marsh Gas, CH_4, is produced in the decomposition of vegetable matter under water, and is given off when the mud at the bottom of stagnant pools is stirred : it also constitutes the "fire-damp" of coal-mines, and is an important constituent of coal gas. It is not formed by direct combination of carbon and hydrogen, but may be prepared by strongly heating a mixture of sodium acetate ($NaC_2H_3O_2$) and sodium hydroxide (caustic soda) with quicklime :

$$NaC_2H_3O_2 + NaOH = CH_4 + Na_2CO_3.$$

It is a colourless gas which burns with a pale scarcely luminous flame. It requires twice its volume of oxygen for combustion, and when mixed with this gas, and exploded in a eudiometer, it yields a quantity of carbon dioxide equal to its own volume :

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$

Pure methane is unaffected by contact with strong sulphuric acid, and is not attacked by chlorine or bromine, unless the mixture is exposed to light. In that case no combination occurs between the marsh gas and the halogen, but the hydrogen of the former is gradually replaced, atom by atom, by equivalent quantities of the latter, with simultaneous formation of hydrogen chloride or bromide. The following series of compounds are formed by chlorine :

Chloromethane, CH_3Cl
Dichloromethane, CH_2Cl_2
Trichloromethane (Chloroform), $CHCl_3$
Tetrachloromethane, CCl_4.

Experiments.—1. Place about 50 grams of crystallised sodium acetate in an evaporating dish, and apply the heat of a Bunsen

burner, stirring the salt continually till all the water of crystallisation has been evaporated. Powder the residual salt when cold, and mix it thoroughly with an equal weight of quicklime and half its weight of solid caustic soda. Place the powder in the iron tube used in preparing hydrogen (p. 22), close one end of this with a cork and adapt to the other end a glass tube to convey away the gas. See that this exit-tube is not obstructed by the powder, and that there is a clear passage over the mixture. This is secured by thrusting a wire or glass rod through the tube before fixing the corks. Place the iron tube upon the small furnace shown in the figure, and apply a gentle heat. The gas must be purified by bubbling through oil of vitriol contained in a small two-necked bottle attached to the generator. It may then be collected in the pneumatic trough.

2. Lift a jar full of the gas from the trough, keeping the mouth downwards; it may be retained under these conditions for some minutes, as it is much lighter than air. Density, 8 (H=1) or ·55 (air=1).

3. Apply a flame to the mouth of the jar; the gas burns giving about the same amount of light as spirit of wine.

4. Mix over water marsh-gas with an equal volume of chlorine. No immediate change occurs in ordinary daylight, and on shaking up the mixture with water, or better, with solution of soda, the chlorine is dissolved, leaving the marsh-gas unchanged.

Ethylene or **Olefiant Gas**, C_2H_4.—This gas is present in small quantity in coal-gas, and is formed during the destructive distillation of many organic substances. It is usually obtained by heating common alcohol with an excess of strong sulphuric acid, whereby the alcohol is deprived of the elements of water:

$$\underset{\text{Alcohol.}}{C_2H_6O} = C_2H_4 + H_2O\,.$$

This change is, however, brought about by two stages, which may be represented by the following equations:

$$\underset{\text{Alcohol.}}{C_2H_6O} + H_2SO_4 = \underset{\substack{\text{Ethyl-hydrogen}\\\text{sulphate.}}}{C_2H_5HSO_4} + H_2O\,.$$

$$\underset{\substack{\text{Ethyl-hydrogen}\\\text{sulphate.}}}{C_2H_5HSO_4} = \underset{\text{Ethylene.}}{C_2H_4} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4}\,.$$

Ethylene is a colourless gas which burns in the air with a highly luminous flame. Mixed with excess of oxygen, and fired, it consumes three times its volume of that gas, and yields twice its own volume of carbon dioxide, thus:

$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O\,.$$

Ethylene is distinguished from marsh gas by being absorbed freely by hot oil of vitriol, producing ethyl-hydrogen sulphate; also by its

combination with chlorine and with bromine, forming the compounds $C_2H_4Cl_2$ and $C_2H_4Br_2$. The former has long been known as 'Dutch liquid,' and from its immiscibility with water, it was formerly regarded as a kind of oil. Hence the name 'olefiant' for the gas. Ethylene can be liquefied at 0° by a pressure of 41 atmospheres. Liquid ethylene boils under common atmospheric pressure at $-103°$, and by its evaporation under reduced pressure a temperature of $-140°$ has been obtained. It has been much used in experiments upon the liquefaction of other gases, especially oxygen, nitrogen, and air.

Experiments with Ethylene.—1. Into a flask provided with funnel-tube and exit-tube for gas (an apparatus similar to that employed in making chlorine, p. 56), pour 25 cubic centimetres of strong spirit of wine and add slowly 50 cc. of strong sulphuric acid, shaking them together. The mixture becomes very hot, and may boil if the acid is added too quickly. Set up the flask over a lamp and connect the exit with a tube for conveying the gas into the pneumatic trough. Apply heat to the flask, and when the mixture boils freely, collect several jars of the gas. The mixture in the flask soon blackens, and the gas is accompanied by a little sulphurous oxide.

2. Ethylene is nearly as heavy as air. Density, 14 ($H=1$) or ·97 ($air=1$). Light the gas at the mouth of one of the jars: it burns with a flame about equal in luminosity to coal-gas.

3. Introduce into a tall cylinder filled with water, standing inverted in the trough, one-third of its volume of ethylene, and then an equal quantity of chlorine. The two gases immediately unite, forming drops of a heavy oil, 'Dutch liquid,' which may be collected in a dish placed beneath. The water therefore quickly rises in the jar and the gases disappear.

HOMOLOGOUS SERIES.

The compounds of carbon with hydrogen alone, or associated with other elements, are very numerous, but their study is much facilitated by the fact that they admit of being classified into series, the several members of which present the same general features. Thus acetylene, marsh gas, and ethylene, the compounds just described, are merely the first terms of three separate series of 'hydrocarbons,' each characterised by peculiarities of its own. The series to which marsh gas, for example, belongs is composed of substances all of which, like marsh gas, are distinguished by a remarkable indifference to chemical agents, being for the most part unaffected by sulphuric acid, and attacked with difficulty by chlorine, by bromine, and by nitric acid. Hence this series of compounds has received the name 'paraffin,' a name originally applied only to one member of the series, a solid substance, in reference to its chemical inactivity (*parum affinis*).

In such a series of closely related compounds of carbon and hydrogen, it is observed (1) that there is a definite relation as regards

composition among the members of such a series, so that the whole may be expressed by a general formula, and that there is a common difference, always amounting to CH_2, in passing from one term to the next. The general formula of the paraffin series is C_nH_{2n+2}, that of the olefine series is C_nH_{2n}. (2) There is a manifest but gradual change of physical properties in ascending such a series, the lower terms being often gaseous, always more volatile than the higher terms, and with rise of boiling point there is noticeable increase of density, and ultimate solidification, with gradually decreasing fusibility. With these changes of physical properties there is generally a modification of chemical characters, the more complex molecules being more sluggish than the lighter and more quickly moving molecules, while at the same time presenting a greater number of points of attack. The character of a homologous series is well illustrated by the paraffins which are given below:

Paraffins, C_nH_{2n+2}.

Name.	Formula.	Boiling Point.
Methane, . . .	CH_4	Gas
Ethane, . . .	C_2H_6	Gas
Propane, . . .	C_3H_8	Gas
Tetrane, . . .	C_4H_{10}	1°
Pentane, . . .	C_5H_{12}	36°
Hexane, . . .	C_6H_{14}	68·5°
Heptane, . . .	C_7H_{16}	98°
Octane, . . .	C_8H_{18}	125·5°
Nonane, . . .	C_9H_{20}	149·5°
Decane, . . .	$C_{10}H_{22}$	173°
Undecane, . . .	$C_{11}H_{24}$	194·5°
Dodecane, . . .	$C_{12}H_{26}$	214·5°
Tredecane, . . .	$C_{13}H_{28}$	234°
Hexdecane, . . . etc.	$C_{16}H_{34}$	Solid, m.p. 19·5°, b.p. 287·5°

Coal-Gas.—The manufacture of coal-gas is a branch of industry of great interest and importance.

When pit-coal is subjected to destructive distillation, a variety of products show themselves—permanent gases, steam, and volatile oils, besides a not inconsiderable quantity of ammonia from the nitrogen always present in the coal. The residue is coke. These substances vary very much in their proportions with the temperature at which the process is conducted, the permanent gases becoming more abundant with increased heat, but, at the same time, losing much of their value for the purposes of illumination.

The coal is distilled in fire-clay retorts (fig. 90), maintained at a bright red heat, and the volatilised product is conducted into a long

horizontal pipe of large dimensions, always half filled with liquid, into which the extremity of each separate ascension tube dips; this is called the *hydraulic main*. The gas and its accompanying vapours are next made to traverse *condensers*—usually a series of iron pipes, or boxes exposing a large surface to the air; here the condensation of the tar and the ammoniacal liquid becomes nearly complete, and

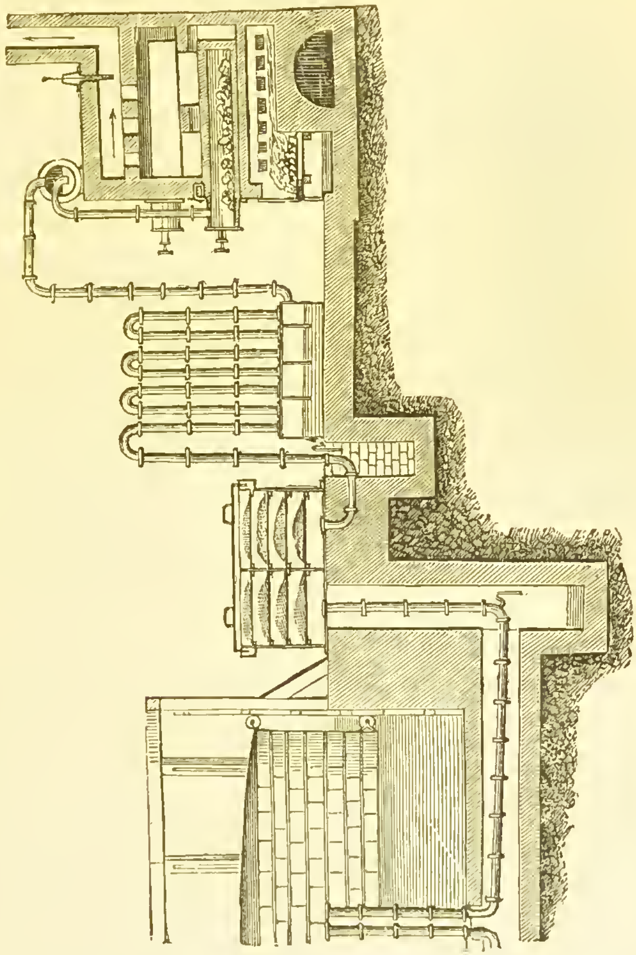
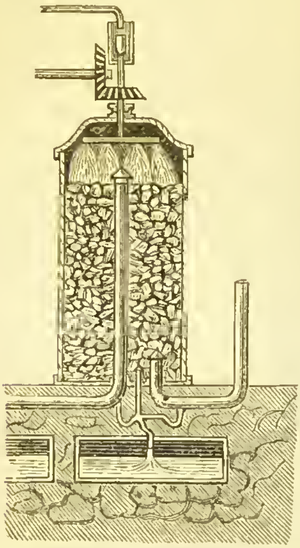


Fig. 90.

the gas is drawn forwards by means of an exhausting pump, and proceeds onwards to another part of the apparatus, in which it is deprived of the sulphuretted hydrogen and carbon dioxide always present in the crude product. This is effected partly in *scrubbers*, partly in *purifiers*. The former (fig. 91) are either tower-like structures, from 70 to 80 feet high and from 10 to 20 feet diameter, filled with coke over which a stream of water trickles, or they consist

of a series of closed chambers supplied with water in which a shaft carrying a number of thin iron disks revolve, thus exposing a large area of freshly wetted surface to the gas as it passes through the chambers. This washing with water removes the last portions of ammonia, and at the same time some of the sulphuretted hydrogen and carbon dioxide. The final removal of these latter compounds was formerly effected by slaked lime, which readily absorbs them. It is, however, now customary to remove the sulphuretted hydrogen by means of hydrated peroxide of iron before bringing the gas into contact with lime for the removal of the carbon dioxide. These materials are placed in the purifiers, which consist of rectangular cast-iron boxes about six feet deep, furnished with a moveable lid (fig. 90). The first series of purifiers is charged with hydrated peroxide of iron placed on wooden perforated trays. After a time the oxide, being reduced to ferrous oxide, ceases to be effective, but on being turned out and exposed to the air absorbs oxygen and regains the power of destroying sulphuretted hydrogen. The principal changes which occur are represented in the two following equations:—

Fig. 91.



$$Fe_2O_3 + H_2S = Fe_2O_2 + H_2O + S$$
$$Fe_2O_2 + O = Fe_2O_3.$$

In this way the same oxide is used over and over again about sixteen times, till the amount of deposited sulphur is considerable. The last of the series of purifiers is charged in the same way with slaked lime which becomes converted into carbonate. The purified gas is then measured by a *meter* of suitable dimensions, and is stored in the *gas-holders* for use.

In order to regulate the pressure of the gas in the main pipes, by which it is distributed according to the demand, a *governor* is used. This is a miniature gas-holder, which actuates a conical valve by means of which the flow of gas is promoted or checked automatically.

Coal-gas varies somewhat in composition and illuminating power. The purified gas contains the following substances, which may be classified into three principal groups:—

1. *Combustible Non-illuminating Gases.*

Hydrogen, H_2, about 40 to 50 per cent.
Marsh-gas, CH_4, about 40 per cent.
Carbonic oxide, CO, about 5 per cent.

2. *Illuminating Constituents.*

$$\left.\begin{array}{l}\text{Ethylene, } C_2H_4\text{, etc.,}\\ \text{Acetylene, } C_2H_2\text{,}\\ \text{Benzene, } C_6H_6\text{, etc.,}\end{array}\right\}\text{ about 5 per cent.}$$

3. *Impurities.*

Nitrogen chiefly derived by leakage from the air. Traces of oxygen, carbon dioxide, vapour of carbon bisulphide, etc.

From this it will be seen that coal-gas consists chiefly of a mixture of hydrogen and marsh-gas, and that its illuminating power is due to the presence of small quantities of vapours rich in carbon. Of these benzene is the most important.

Oil-Gas and Water-Gas.—A valuable illuminating gas may be prepared from oil, by dropping it into a red-hot iron retort filled with coke ; the liquid is in great part decomposed and converted into permanent gas, which requires no purification, as it is quite free from the ammoniacal and sulphur compounds which vitiate gas from coal. This gas was at one time prepared in London for general illuminating purposes ; it was compressed for the use of the consumer into strong iron vessels, to the extent of 30 atmospheres ; but the manufacture has been for ordinary purposes superseded in this country by gas from coal. Oil-gas is, however, still made on a considerable scale in apparatus of improved form, but it is now applied chiefly for the purpose of improving the illuminating power of coal-gas to which it is added. It is also used for special purposes, such as the lighting of railway carriages.

In the United States much gas is made by the action of steam upon red-hot coke. This consists of a mixture of carbonic oxide and hydrogen :

$$H_2O + C = H_2 + CO.$$

It is rendered suitable for purposes of illumination by mixing it with vapour of mineral naphtha. A serious objection to the use of this gas in houses arises from the poisonous character of carbonic oxide and the consequent danger from escape.

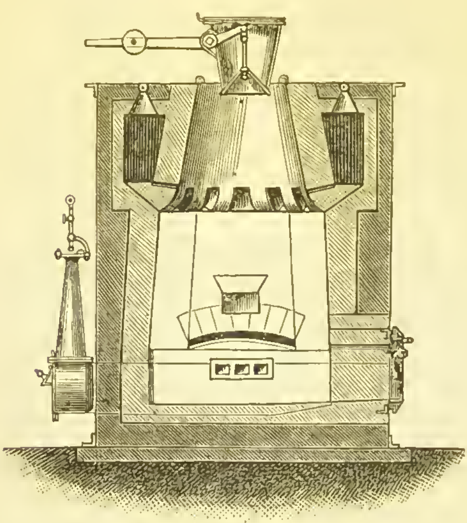
Producer Gas.—When coal is heated in a closed chamber into which air is admitted in quantity just sufficient to maintain the combustion, its carbonaceous constituents are entirely converted into gas, the residue consisting only of incombustible mineral ash.

A gas of this kind contains about one-third of its volume of carbonic oxide, mixed with nitrogen derived from the air and a little carbon dioxide, etc. The chambers in which this operation is conducted are called "*Gas Producers*," and are arranged so that the coal and air may be supplied without interruption of the process.

The gas is extensively used for industrial purposes, for heating boilers, melting iron and steel, and in many other manufacturing operations.

One form of gas producer which is much used is represented in section in the accompanying figure. The coal is introduced through the hopper at the top into a cylindrical chamber constructed of firebrick, through the bottom of which is blown a sufficient supply of air by means of a steam-jet, which is discharged into the open mouth of the trumpet-shaped injector at the side. The gases, which, when steam is used, contain a considerable proportion of hydrogen, pass through the apertures shown in the upper part of the producer into an annular chamber, of which two sections are shown, which encircles the upper part of the structure. From this chamber the gases pass by means of a wide pipe at the side to the furnace where they are to be burnt.

Fig. 92.



Compounds of Carbon with the Halogen Elements.—Several compounds of carbon and chlorine are known, viz., C_2Cl_4, C_2Cl_6, CCl_4, and C_6Cl_6, and similar compounds with bromine and iodine.

Carbon Tetrachloride, CCl_4.—This is the most important of the compounds of carbon with a halogen. It is produced, as already mentioned, when marsh-gas mixed with excess of chlorine is exposed to sunlight, but it is always manufactured by the action of chlorine upon carbon bisulphide. Chlorine mixed with the vapour of that substance is passed through a red-hot tube and then into a condenser. The liquid is purified by shaking it with lime and water and redistillation :

$$CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2.$$

Carbon tetrachloride is a colourless liquid of specific gravity 1·6 and it boils at 77°. It has a peculiar heavy smell resembling that of chloroform. It is insoluble in water, but mixes with alcohol, ether, and benzene. It does not dissolve salts but takes up bromine and iodine freely and without chemical change.

COMPOUNDS OF CARBON AND OXYGEN.

There are two compounds of carbon and oxygen, in which the quantities of oxygen united with the same amount of carbon are to each other as 1 : 2, namely,

	Formula.	Composition by weight. Carbon.	Oxygen.
Carbon Monoxide,	CO	3	4
Carbon Dioxide,	CO_2	3	8

Carbon Monoxide, *Carbonic Oxide.*—When carbon dioxide is passed over red-hot charcoal or metallic iron, one-half of its oxygen is removed, and it becomes converted into carbon monoxide. The blue flame often seen playing upon the surface of a clear fire is produced by carbon monoxide in the act of burning into carbon dioxide.

Experiment.—Introduce into a flask fitted with a bent tube some crystallised oxalic acid ($H_2C_2O_4.2H_2O$), and pour upon it five or six times as much strong oil of vitriol. On heating the mixture, the oxalic acid is resolved into water, carbon dioxide, and carbon monoxide : $H_2C_2O_4 = CO + CO_2 + H_2O$: and by passing the gases through a strong solution of caustic potash, the first is withdrawn by absorption, while the second remains unchanged. The apparatus employed in the preparation of hydrochloric acid (p. 99) may be used, the washing bottle being half filled with solution of potash.

Experiment.—Another and perhaps preferable method, is to substitute sodium formate for the oxalic acid in the previous experiment. Pure carbon monoxide is obtained :

$$\underset{\text{Formic Acid.}}{HCHO_2} - H_2O = CO,$$

and the potash may therefore be dispensed with.

A third method is to heat finely-powdered yellow potassium ferrocyanide with 8 or 10 times its weight of concentrated sulphuric acid. The salt is entirely decomposed, yielding a copious supply of perfectly pure carbon monoxide, which may be collected over water in the usual manner. The reaction is represented by the equation—

$$\underset{\substack{\text{Potassium ferro-}\\\text{cyanide.}}}{K_4FeC_6N_6} + 6H_2O + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{6H_2SO_4} = 6CO + \underset{\substack{\text{Potassium}\\\text{sulphate.}}}{2K_2SO_4} +$$

$$\underset{\substack{\text{Ammonium}\\\text{sulphate.}}}{3(NH_4)_2SO_4} + \underset{\substack{\text{Ferrous}\\\text{sulphate.}}}{FeSO_4}.$$

Carbon monoxide is a combustible gas, which burns with a beautiful pale-blue flame, generating carbon dioxide. It is colourless, has very little odour, is but slightly soluble in water, and is extremely poisonous. Mixed with oxygen, it explodes by the electric spark, but

only in the presence of moisture. Its density is 14 (H=1) or 0·973 (air=1); a litre weighs 1·2515 grams; 100 cubic inches weigh 30·21 grains.

The relations by volume of the oxides of carbon are as follows:—Carbon dioxide contains its own volume of oxygen, that gas suffering no change of bulk when carbon is burnt in it. One measure of carbon monoxide, mixed with half a measure of oxygen and exploded, yields one measure of carbon dioxide: hence carbon monoxide contains half its volume of oxygen.

Experiments.—1. Ignite the gas as it issues from the delivery-tube, notice the peculiar blue colour of the flame.

2. Collect a jar full of the gas from the formate, pour into it some clear lime-water and shake it up. The lime-water remains clear. Now ignite the gas at the mouth of the jar and let it burn out: on shaking up the lime-water a white precipitate of calcium carbonate is immediately formed. If in this experiment the gas be prepared from oxalic acid, it must be left in contact with caustic potash for a short time to remove the last portions of carbon dioxide.

Carbon monoxide unites with chlorine under the influence of light, forming a pungent, suffocating compound, called phosgene gas, or carbonyl chloride, $COCl_2$. Carbon monoxide is also absorbed by a solution of cuprous chloride forming the compound Cu_2Cl_2CO; this fact is turned to account in the analysis of mixtures of gases. Though this oxide is not absorbed, like the dioxide, by solution of caustic potash at common temperatures it is taken up at a temperature of about 100° and is converted into a formate, thus:

$$KHO + CO = KCHO_2.$$

Its most remarkable compound, however, is that which is formed by passing it over finely divided metallic nickel gently heated. The product is a volatile compound having the composition $Ni(CO)_4$, which is readily condensed into a colourless mobile liquid. A similar compound $Fe(CO)_5$ is formed, though less easily, with metallic iron.

Carbon Dioxide, or **Carbonic Anhydride,** *Carbonic Acid Gas,* CO_2.—This compound is always produced when charcoal or any other form of carbon burns in air or oxygen gas. It is also formed in large quantity in the decomposition of limestone in the lime kiln, also in the process of fermentation in the brewers' vat, and from both these sources large quantities are now collected for manufacturing purposes. It is, however, more conveniently prepared for purposes of experiment by decomposing a carbonate with one of the stronger acids.

Experiment.—For this purpose the apparatus for generating hydrogen (p. 23) may again be employed: fragments of marble are put into the bottle with enough water to cover the extremity of the

funnel-tube, and hydrochloric or nitric acid is added by the latter, until the gas is freely disengaged :

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

Chalk-powder and dilute sulphuric acid may be used instead :

$$CaCO_3 + H_2SO_4 = CaSO_4 + H_2O + CO_2.$$

This latter process is less convenient than the former because the calcium sulphate produced is but slightly soluble and is soon deposited so as to give rise to a pasty mass.

The gas may be collected over water, although with some loss; or very conveniently by displacement of air, if it be required dry, or in the mercurial trough. The moisture present in the gas may be removed by causing it to pass through a tube containing pumice wetted with sulphuric acid, or merely to bubble through the acid contained in a bottle with two necks.

Carbon dioxide is a colourless gas having an agreeable pungent taste and odour. Its density is 22 ($H = 1$) or 1·524 ($air = 1$); a litre weighs 1·96664 grams, and 100 cubic inches weigh 47·26 grains. It is very hurtful to animal life, even when largely diluted with air, acting as a narcotic poison : hence the danger arising from imperfect ventilation, the use of fire-places and stoves of all kinds unprovided with proper chimneys, and the crowding together of many individuals in houses and ships without efficient means of renewing the air : for carbon dioxide is constantly disengaged during the process of respiration, which, as already mentioned, is nothing but a process of slow combustion. This gas is sometimes emitted in large quantity from the earth in volcanic districts, and it is constantly generated where organic matter is in the act of undergoing fermentative decomposition. The fatal "after-damp" of the coal-mines contains a large proportion of carbon dioxide.

A lighted taper plunged into carbon dioxide is instantly extinguished even to the red-hot snuff. The gas, when diluted with three times its volume of air, still retains the power of extinguishing a light. It is easily distinguished from nitrogen, which is also incapable of supporting combustion, by its rapid absorption by caustic alkali, or by lime-water; the turbidity communicated to the latter from the production of insoluble calcium carbonate is very characteristic.

Cold water dissolves about its own volume of carbon dioxide, whatever be the density of the gas with which it is in contact (comp. p. 83); the solution temporarily reddens litmus paper. Common soda water and effervescent wines afford examples of the solubility of the gas. Even boiling water absorbs a perceptible quantity.

Carbon dioxide is liquefied by a pressure of 38·5 atmospheres at 0°. The liquefied oxide is colourless and limpid, lighter than water, and four times more expansible than air; it mixes in all proportions with ether, alcohol, naphtha, oil of turpentine, and carbon bisul-

phide, and is insoluble in water and fat oils. In this condition it does not exhibit any of the properties of an acid.

When the liquid is allowed to escape through a fine jet into the air a portion of it evaporates so rapidly as to cause a great reduction of temperature sufficient to produce solidification of the remainder. The product is collected either in a drum-shaped metal box or in a flannel bag. In this condition carbon dioxide is a white snow-like substance which is a bad conductor for heat, and, therefore, may be preserved in the air for some time. It evaporates into gas without liquefying. When dissolved in common ether the liquid acquires a temperature of about $-77°$, under atmospheric pressure, or it may fall to $-103°$ when boiling under reduced pressure. Such a mixture was first employed by Faraday to obtain low temperatures in his experiments upon the liquefaction of gases, and is now frequently used for similar purposes.

Experiments.—1. Immerse a lighted taper in carbonic acid gas; it is instantly extinguished.

2. Into a jar of the gas pour some clear lime-water; a white precipitate of calcium carbonate is formed in the liquid.

3. Attach a small candle to a wire and lower it into a small jar of air; then take a jar full of carbonic dioxide and tilt it over the candle as in pouring a liquid. The carbon dioxide is heavy enough to flow from one vessel to the other, and its presence is indicated by the extinction of the flame.

4. Place a few fragments of caustic potash in a small U-tube and weigh the tube with its contents. Then attach it to the carbonic acid apparatus and allow the gas to flow through the tube for a few minutes. Weigh again and observe that there is an increase of weight. Dissolve the potash in a little water placed in a small gas cylinder and add excess of any acid. Effervescence occurs, and the cylinder, if not too large, is filled with carbonic dioxide, which may be recognised by a burning taper.

Carbon dioxide exists, as already mentioned, in the air: relatively its quantity is but small: but absolutely, taking into account the vast extent of the atmosphere, it is very great, and fully adequate to the purpose of supplying plants with their carbon, these latter having the power, by the aid of their green leaves, of decomposing carbon dioxide, retaining the carbon, and expelling the oxygen. The presence of light is essential to this effect, but the manner of its production is not yet clearly understood.

The carbonates form a very large and important group of salts, some of which, as the carbonates of calcium and magnesium, occur very abundantly in nature. They contain the elements of carbon dioxide and a metallic oxide: calcium carbonate, for example, being represented by the formula CaO,CO_2 or $CaCO_3$; but they are never formed by the direct union of dry carbon dioxide with a dry metallic oxide, the intervention of water being always required to bring about the combination. Potassium carbonate (pearl-ash) is the chief constituent of wood-ashes: sodium carbonate is contained in the ashes

of marine plants, and is manufactured on a very large scale by heating sodium sulphate with lime and coal. These carbonates are soluble in water. The other metallic carbonates, which are usually insoluble, may be formed by mixing a solution of potassium or sodium carbonate with a soluble metallic salt; thus, when solutions of lead nitrate and sodium carbonate are mixed together, the lead and sodium change places, forming sodium nitrate, which remains dissolved, and lead carbonate, which, being insoluble in water, is precipitated as a white powder: $Pb(NO_3)_2 + Na_2CO_3 = 2NaNO_3 + PbCO_3$.

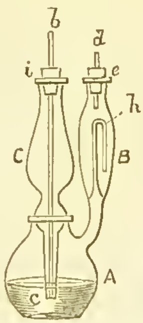
The solution of carbon dioxide in water may be supposed to contain hydrogen carbonate or carbonic acid, H_2CO_3 or H_2O,CO_2; but this compound is not known in the separate state, only in aqueous solution. According to Wroblewski, however, carbon dioxide unites with water at 0° C. and under a pressure of about 16 atmospheres, forming the hydrate $CO_2,8H_2O$ or $H_2CO_3.7H_2O$.

Experiments.—1. Allow carbon dioxide gas to bubble through some distilled water contained in a flask, to which a few drops of blue litmus solution have been added. The liquid soon acquires a wine-red tint.

2. Boil the solution for a few minutes, and observe that the blue colour is gradually restored, in consequence of the expulsion of the carbonic anhydride.

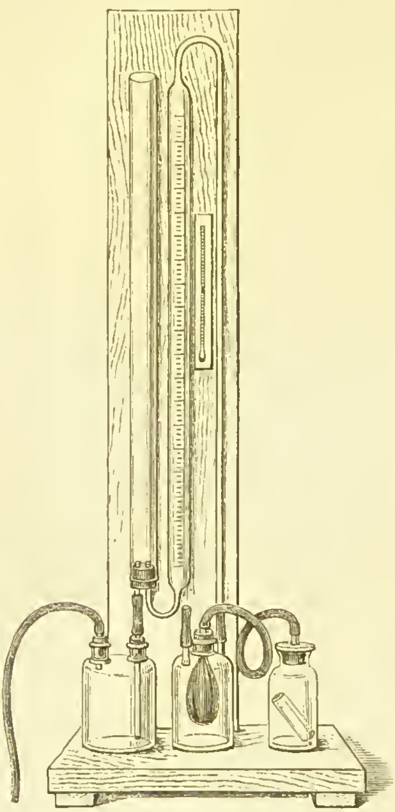
The amount of carbon dioxide contained in a carbonate may be estimated by the loss of weight which the salt undergoes when decomposed by an acid. This may be determined by means of Geissler's or some similar apparatus (fig. 93). It consists of three glass vessels, A, B, C, the last of which is ground air-tight into the neck of A; *b c* is a glass tube open at both ends, ground water-tight into C at the lower end, and kept in position by the cork *i*, which can slide up and down on the tube *b c*. The cork *e* must close air-tight in B, and the tube *d* in *e*. The weighed substance to be decomposed is introduced into A, and water is added. The vessel C is then filled with the aid of a pipette nearly to the top with dilute nitric or hydrochloric acid, the cork *i* having been previously moved upwards without raising the tube *b*. The cork *i* is then replaced; the vessel C again inserted into A; the vessel B is rather more than half filled with strong sulphuric acid; and the tube *b* is closed at the top by placing over it a small piece of caoutchouc tubing, with a glass rod fitted into the other end. The apparatus having been weighed, the decomposition of the carbonate is effected by opening the tube *b* a little, so as to cause acid to pass from C into A. The carbon dioxide then passes through the bent tube *h* into the sulphuric acid, by which it is dried, and finally leaves the apparatus through *d*. When the decom-

Fig. 93.



position is complete, the vessel A is gently heated, the stopper is removed from *b*, and the carbon dioxide still remaining in the apparatus is sucked out at *d*. The apparatus, after cooling, is again weighed, and the difference between the two weighings gives the weight of the carbon dioxide expelled.

Fig. 94.



For many purposes, however, it is more convenient and almost equally accurate to estimate the volume of the gas expelled by the decomposition of the carbonate by an acid. Fig. 94 represents Scheibler's apparatus which is used for this purpose. The carbonate is weighed out in a little bottle into which may be lowered a tube filled with dilute hydrochloric acid. Through the stopper of the bottle passes one extremity of a flexible tube, the other end of which is united to a toy india-rubber balloon enclosed in the second bottle. When the acid is poured out upon the carbonate by inclining the first bottle the escaping gas inflates the balloon and so drives the water out of the measuring tube. The level of the water in the two tubes must be adjusted before and after each evolution of gas, the volume of which can then be easily read off. The temperature is given by the thermometer attached to the stand.

Carbonyl Chloride, Carbon Oxychloride, or **Phosgene,** $COCl_2$. —This compound is the product, already referred to, obtained when a mixture of carbon monoxide and chlorine is exposed to sunshine. It is also formed without the aid of light by passing the mixed gases through a long tube filled with crushed animal charcoal or bone black.

It is produced most freely by passing the gases together through boiling antimony pentachloride which causes them to unite at once. The product is purified from excess of chlorine by passing through a tube filled with powdered antimony.

Carbonyl chloride at the temperature of the air is a colourless gas but it may easily be liquefied, and the liquid boils at 8°. Brought

into contact with water it is decomposed into carbonic acid and hydrogen chloride:

$$COCl_2 + 2H_2O = CO(HO)_2 + 2HCl.$$

The carbonic acid is as usual resolved at once into water and carbon dioxide:

$$CO(HO)_2 = CO_2 + H_2O.$$

When carbonyl chloride is mixed with ammonia it forms the amide of carbonic acid, a substance which is identical with urea, an excretory product of the animal body. Sal-ammoniac is produced at the same time:

$$COCl_2 + 2NH_3 = \underset{\text{Carbamide.}}{CO(NH_2)_2} + 2HCl.$$

Carbonyl chloride stands therefore in the same relation to the hypothetical carbonic acid as sulphuryl chloride to sulphuric acid and phosphoryl chloride to phosphoric acid, and its known composition affords additional evidence in favour of the formula H_2CO_3 or $CO(HO)_2$, usually assigned to carbonic acid.

Carbon and Sulphur.

Two compounds of these elements are known, viz., the bisulphide produced by the direct combination of its elements at a high temperature, and a monosulphide.

Carbon Bisulphide or **Disulphide**, CS_2.—Charcoal heated to redness in sulphur vapour combines with it and forms a compound which may be condensed to a colourless very inflammable liquid.

For preparation on the large scale, a tubulated earthen retort is filled with charcoal, and the sulphur is dropped in through a porcelain tube passing through the tubulus, and reaching nearly to the bottom; or the charcoal is contained in a large iron cylinder, and the sulphur introduced through a pipe fitted into the lower part.

The vaporised product passes first through an empty two-necked stoneware bottle, for the reception of any uncombined sulphur, and then into a long condenser supplied with water as cold as possible. In summer time the addition of ice will be necessary. The liquid has a very offensive odour, due to sulphurous impurities, which can be only partly removed by distillation. The complete purification of carbon bisulphide is difficult.

Carbon bisulphide is a transparent colourless liquid of great refractive and dispersive power. Its density is 1·272, and that of its vapour is 2·67 (air = 1). It boils at 43°, and emits vapour of considerable pressure at common temperatures. In its ordinary state, it has a very repulsive odour, but when pure it smells somewhat like chloroform. When set on fire in the air, it burns with a blue

flame, forming carbon dioxide and sulphur dioxide ; and when its vapour is mixed with oxygen it becomes explosive. Carbon bisulphide, when heated with water in a sealed tube to about 153°, is converted into carbon dioxide and hydrogen sulphide. In contact with nascent hydrogen (when heated with zinc and dilute sulphuric acid) it is converted into a white crystalline substance, having the composition CH_2S, crystallising in square prisms, insoluble in water, alcohol, and ether, but soluble in carbon bisulphide, subliming at 150°, and decomposing at 200°. Carbon bisulphide freely dissolves sulphur, and by spontaneous evaporation deposits the latter in beautiful crystals ; it also dissolves phosphorus, iodine, camphor, and caoutchouc, and mixes easily with oils. It is extensively used in the vulcanisation of caoutchouc, and in the manufacture of gutta percha ; also for extracting bitumen from mineral substances, and oils from seeds.

Carbon bisulphide must be regarded as the anhydride of a thio-acid to which it stands in the same relation as carbon dioxide to carbonic acid.

Thiocarbonic Acid, $H_2CS_3 = CS(SH)_2$, also called *Sulphocarbonic Acid.*—Thiocarbonates are formed on adding carbon bisulphide to the solution of an alkaline sulphide, *e.g.*, $CS_2 + Na_2S = Na_2CS_3$ or $CS_2 + 2NaHS = Na_2CS_3 + H_2S$. Their production is therefore analogous to that of carbonates which are formed by the union of carbon dioxide and metallic oxides, $CO_2 + Na_2O = Na_2CO_3$ or $CO_2 + 2NaHO = Na_2CO_3 + H_2O$. From the resulting solution, decomposed by hydrochloric acid, thiocarbonic acid may be precipitated in the form of a yellow oil having an offensive and pungent odour, and resolved by heat into CS_2 and H_2S. The thiocarbonates of the alkali-metals and alkaline earth-metals are soluble in water, and the solutions give a brown precipitate with copper salts, yellow with dilute silver nitrate, red with lead-salts. These precipitates readily turn black, from separation of the corresponding sulphides.

Carbon Monosulphide, CS, has been variously described as a gas obtained by heating sodium sulphide with chloroform, $3Na_2S + 2CHCl_3 = H_2S + 2CS + 6NaCl$, and as a solid brown powder formed by the action of sunlight upon carbon bisulphide or by prolonged digestion of iron wire with the same substance.

If both these statements are correct it appears probable that the solid compound is "polymeric" with the gas, and may be represented by such a formula as $(CS)_n$. The subject, however, requires further investigation.

Thiocarbonyl Chloride, $CSCl_2$, is obtained by the prolonged action of dry chlorine gas on carbon bisulphide, and more readily by heating the bisulphide in sealed tubes at 100° with phosphorus pentachloride : $CS_2 + PCl_5 = PSCl_3 + CSCl_2$. It is a colourless strong-smelling liquid, insoluble in water, boiling at 70°.

Carbon Oxysulphide, or Carbonyl Sulphide, COS.—This compound appears to exist in some sulphur springs and in the sulphurous gases of volcanoes. It is produced by direct combination when carbon monoxide mixed with sulphur-vapour is passed through a red-hot porcelain tube. As thus prepared it is mixed with free carbon monoxide; but on passing the gas through alcoholic potash, the oxysulphide is alone absorbed, and may be liberated in the pure state by treating the solution with hydrochloric acid.

Carbon oxysulphide is also produced by gently heating the bisulphide with an equivalent quantity of sulphur trioxide: $CS_2 + SO_3 = CSO + SO_2 + S$; and by decomposing potassium thiocyanate with moderately dilute acids: thiocyanic acid, HCNS, is then liberated and decomposed by the water present in the manner represented by the equation, $HCSN + H_2O + HCl = NH_4Cl + COS$.

Carbon oxysulphide is a gas of density 2·1, and may easily be poured from one vessel to another. It has an aromatic odour like that of some resins, slightly also that of hydrogen sulphide, and a feebler acid reaction than carbon dioxide. At a low red heat it is partly resolved into carbon monoxide and sulphur-vapour; by a fine platinum wire ignited by the electric current, it is slowly but completely decomposed, yielding an equal volume of carbon monoxide. It burns in the air with a faint blue flame, producing carbon dioxide and sulphur dioxide; with $1\frac{1}{2}$ volume of oxygen it forms an explosive mixture burning with a shining bluish-white flame.

Water absorbs about its own volume of carbon oxysulphide, acquiring a sweetish and afterwards a pungent taste, and decomposing it after some time. Potash solution absorbs the gas as completely as carbon dioxide, though less quickly; the solution exhibits the reactions of metallic sulphides, and when treated with acids gives off hydrogen sulphide and carbon dioxide. Baryta-water and lime-water act in a similar manner. Neutral or acid solutions of lead, copper, cadmium, and silver salts are not precipitated by the gas, but when mixed with excess of ammonia they yield with it characteristic precipitates of metallic sulphides.

Carbon and Nitrogen.

Cyanides.—When nitrogen is brought into contact with potassium carbonate mixed with carbon at a bright red heat, the nitrogen of the air unites with the carbon and the potassium forming a compound called a cyanide:

$$K_2CO_3 + 4C + N_2 = 2KCN + 3CO.$$

The production of this compound is often observed in the joints of the blast furnace (see Iron), owing to the action of atmospheric nitrogen upon the mixture of carbon and the alkaline constituents of the coal ashes.

Potassium cyanide is usually manufactured by heating strongly

animal refuse such as scraps of wool, hair, hide, or hoof, all of which are rich in nitrogen as well as carbon, together with potassium carbonate and scrap-iron in an iron pot. On treating the residual fused mass with water, a complex salt is dissolved out called yellow prussiate of potash or potassium ferro-cyanide, which crystallises in beautiful quadratic tables and prisms, and has the formula $K_4FeC_6N_63H_2O$. This compound dried and heated alone is resolved into iron, carbon, nitrogen, and potassium cyanide. The last named compound is obtained more economically by fusing potassium ferro-cyanide with dry potassium carbonate :

$$K_4FeC_6N_6 + K_2CO_3 = \underset{\text{Cyanide.}}{5KCN} + \underset{\text{Cyanate.}}{KCNO} + CO_2 + Fe.$$

This is a commercial process by which large quantities of cyanide are made. The presence of the cyanate does not interfere with the use of the salt in the manufacturing operations to which it is applied.

Another process by which cyanides are manufactured is based upon the interaction which ensues when carbon bisulphide is heated with ammonia, whereby a thiocyanate and a sulphide are formed :

$$CS_2 + 4NH_3 = NH_4CNS + (NH_4)_2S.$$

If an alkali, such as caustic soda, and peroxide of iron or manganese are present, the whole of the ammonia is converted into sodium thiocyanate, while a sulphide of iron or manganese is precipitated. From the thiocyanate, by heating it with iron turnings, the sulphur is withdrawn, and a cyanide, NaCN, is obtained. Alkaline cyanides have of late years acquired great importance from their extensive use in the extraction of gold from silicious rocks.

Hydrogen Cyanide, *Hydrocyanic Acid,* often called *Prussic Acid,* HCN.—When either ferro-cyanide or cyanide of potassium is distilled with dilute sulphuric acid a volatile compound is obtained called hydrocyanic or prussic acid, HCN. If ferro-cyanide is employed, the changes which occur result in the formation of an insoluble double ferro-cyanide, which, together with the sulphate, remains in the residue :

$$\underset{\substack{\text{Potassium}\\\text{ferro-cyanide.}}}{2K_4FeC_6N_6} + 6H_2SO_4 = \underset{\substack{\text{Hydrogen}\\\text{cyanide.}}}{6HCN} + 6KHSO_4 + \underset{\substack{\text{Potassio-ferrous}\\\text{ferro-cyanide.}}}{K_2FeFeC_6N_6}.$$

Hydrogen cyanide when pure is a colourless liquid which boils at 26·5°, and is probably the most poisonous substance known. It has the properties of an acid, interacting with alkalis and dissolving many metallic oxides to form a series of salts which in general resemble the chlorides. Thus potassium cyanide, KCN, crystallises from water in cubes like potassium chloride, KCl ; silver cyanide, AgCN, is a white curdy precipitate resembling silver chloride, AgCl ;

mercuric cyanide, $Hg(CN)_2$, crystallises in prisms similar to those of mercuric chloride, $HgCl_2$. The cyanides of the heavy metals are, however, decomposed by heat more easily than the corresponding chlorides.

Cyanogen, C_2N_2.—When dry mercuric cyanide is strongly heated in a glass tube, fitted up like that used for the evolution of oxygen (p. 37), it splits up into metallic mercury, and a gaseous body called c y a n o g e n, containing 12 parts by weight of carbon to 14 of nitrogen, and represented by the formula C_2N_2. It must be collected over mercury, as it is rapidly absorbed by water.

Cyanogen is a colourless gas, having a pungent and a very peculiar odour, remotely resembling that of peach-kernels. Exposed while at the temperature of 7·2° C. to a pressure of 3·6 atmospheres, it condenses to a thin, colourless, transparent liquid. It is inflammable, and burns with a beautiful purple or peach-blossom-coloured flame, generating carbon dioxide and liberating nitrogen. Its density is 1·801 referred to air, or 26 referred to hydrogen as unity. One volume of it exploded with 2 volumes oxygen, yields 1 volume nitrogen and 2 volumes carbon dioxide. Now, the weights of equal volumes of cyanogen, nitrogen, and carbon dioxide, are as 26 : 14 : 22. Consequently, 26 parts by weight of cyanogen yield by combustion 14 parts of nitrogen and 44 parts of carbon dioxide, containing 12 parts of carbon; or 26 cyanogen = 12 carbon + 14 nitrogen.

This group of elements, represented by the formula CN, which combines with elementary bodies, and is capable of passing from one state of combination to another, just as if it were itself an elementary body, affords an example of what is called a c o m p o u n d r a d i c l e.

When mercuric or silver cyanide is heated it will be observed that a considerable quantity of a nearly black substance is formed together with the residual metal. This substance has the same composition as the gas, and has received the name *paracyanogen*. The formula may be written $(CN)_n$, but the degree of condensation is not known, and no value can be assigned to the n. Heated to redness, paracyanogen is completely converted into cyanogen gas.

SILICON AND BORON.

These two elements, though differing in their capacity of combination as shown by the formulæ of their compounds, have many characters in common. They both occur in several allotropic modifications, they form unstable gaseous compounds with hydrogen, each forms one solid, fusible, non-volatile oxide, and their chlorides which are volatile, colourless liquids are both decomposed by contact with water.

Silicon is often ranged along with carbon on account of its combination with four atoms of hydrogen or of chlorine, but its compounds are almost uniformly unlike the corresponding compounds of carbon, the oxide for example $(SiO_2)_n$ being a crystalline non-volatile solid, while carbon dioxide is so exceedingly volatile as to be gaseous under all ordinary conditions.

SILICON.

Symbol, Si. Atomic weight, 28.

This element in union with oxygen forms silica, or the earth of flints (*Silex*), which is one of the most abundant of natural minerals either in the crystallised form as quartz, in its several varieties, or as a constituent of numerous silicates. It is also abundant in the ashes of many plants.

To obtain silicon in the free state, potassium silicofluoride is heated in a covered crucible with nearly its own weight of metallic sodium, whereupon violent reaction ensues, resulting in the formation of sodium and potassium fluorides and free silicon. On transferring the contents of the tube to cold water, the fluorides dissolve, and silicon remains behind. Silicon may also be obtained direct from quartz sand by heating it strongly with four times its weight of magnesium powder. On treating the resulting mass with hydrochloric acid, some silicon hydride is evolved as gas, and the silicon is left insoluble in the amorphous state.

Silicon thus prepared is a dark-brown powder, destitute of lustre. Heated in the air, it burns, and becomes superficially converted into silica. It is also acted upon by sulphur and by chlorine. When silicon is strongly heated in a covered crucible, its properties are greatly changed; it becomes darker in colour, denser, and incombustible, refusing to burn even when heated by the flame of the oxy-hydrogen blow-pipe.

Silicon, like carbon and boron, is capable of existing in several allotropic modifications. The modification above mentioned is amorphous. The crystalline modification may be obtained by melting the amorphous silicon with metallic zinc, and dissolving

out the excess of zinc from the mass when cold, or by introducing into a red-hot crucible a mixture of 3 parts of potassium silicofluoride, 1 part of sodium in small fragments, and 4 parts of granulated zinc, and heating to perfect fusion. On slowly cooling, there is formed a button of zinc, covered and interspersed with needle-shaped crystals, consisting of octahedrons joined in the direction of the axis. This crystallised silicon, which may be readily freed from zinc by treatment with acids, resembles crystallised hæmatite in colour and appearance ; it scratches glass, and fuses at a temperature approaching the melting point of cast-iron, and has a specific gravity between 2·3 and 2·4. Silicon in a crystalline state may also be obtained by heating aluminium in a stream of silicon chloride or fluoride. Aluminium chloride or fluoride volatilises leaving a metallic mass containing crystals of silicon.

Silicon Hydride, or *Silicomethane*, SiH_4.—This compound is obtained when a solution of common salt or of sulphuric acid is electrolysed, the negative electrode employed consisting of aluminium containing silicon. The gas is most easily obtained by treating magnesium silicide with hydrochloric acid. Both methods yield silicon hydride mixed with free hydrogen. Pure silicon hydride has been obtained by decomposing triethyl silico-formate with sodium. The reaction by which it is produced is represented by the following equation :

$$\underset{\text{Triethyl silico-formate.}}{4SiH(OC_2H_5)_3} = \underset{\text{Silicic hydride.}}{SiH_4} + \underset{\text{Tetrethyl silicate.}}{3Si(OC_2H_5)_4}.$$

Silicon hydride is a colourless gas, having a density 16 (H = 1). In the impure state, as obtained by the first two processes above given, it takes fire spontaneously on coming in contact with the air, and burns with a white flame, evolving clouds of silica. Pure silicic hydride, however, does not ignite spontaneously under the ordinary atmospheric pressure ; but on passing a bubble of air into the rarefied gas standing over mercury, it takes fire, and yields a deposit of amorphous silicon mixed with silica. When heated to a temperature of about 400° silicon hydride is decomposed into hydrogen and silicon, silicon being deposited. When passed into chlorine gas, it takes fire, forming silicon tetrachloride and hydrochloric acid.

Halogen-Compounds of Silicon.

Silicon Tetrachloride, or *Silicic Chloride*, $SiCl_4$, is formed by direct combination of its elements, but is usually prepared by mixing finely-divided silica with charcoal-powder and oil, strongly heating the mixture in a covered crucible, and then exposing the mass so obtained in a porcelain tube heated to full redness, to the action of perfectly dry chlorine gas. A good condensing arrange-

ment, supplied with ice-cold water, must be connected with the porcelain tube :

$$2Cl_2 + SiO_2 + 2C = SiCl_4 + 2CO.$$

The product is a colourless and very volatile liquid, of relative density 1·524 at 0°, boiling at 50°, and having a pungent, suffocating odour. In contact with water, it yields hydrochloric acid and gelatinous silica.

Silicon Hexchloride, Si_2Cl_6, is formed when the tetrachloride is passed over silicon, heated to whiteness in a porcelain tube. It is a colourless liquid, having a density of 1·58 at 0°, solidifying at −1°, and boiling at 146°; vapour density 9·7. It fumes strongly in the air, and takes fire when heated. It begins to decompose at 350°, and the decomposition goes on at an increasing rate till the temperature rises to 800°, at which point the compound is completely resolved into the tetrachloride and free silicon: $2Si_2Cl_6 = 3SiCl_4 + Si$. If, however, the temperature of the vapour be quickly raised beyond 1000°, no such decomposition takes place.

Silicon Hydrotrichloride, or *Silicic Chloroform*, $SiHCl_3$ (chloroform, $CHCl_3$, having its carbon replaced by silicon), is obtained by passing dry hydrogen chloride over crystallised silicon, heated to a temperature below redness in a porcelain tube. It is a very volatile strong-smelling liquid, which fumes in the air and boils at 42°. It is very inflammable, and burns with a green-edged flame, evolving white clouds of silica. It is readily decomposed by water, with precipitation of a white powder, $Si_2H_2O_3$, called *Silicoformic Anhydride*, formed as shown by the equation: $2SiHCl_3 + 3H_2O = 6HCl + Si_2H_2O_3$. This body is very unstable, and is decomposed by dilute ammonia, yielding silicic acid and hydrogen.

With *bromine* and *iodine*, silicon forms compounds analogous in composition to the chlorine-compounds, and prepared by similar methods :—

$SiBr_4$ is a colourless heavy liquid, boiling at 154°, and solidifying to a crystalline mass at 13°. Si_2Br_6 forms large crystalline tablets, melts when heated, and distils without decomposition at 240°. $SiCl_3Br$, prepared by heating silico-chloroform with bromine at 100°, is a colourless liquid, boiling at 80°.

SiI_4, obtained by direct combination, crystallises from carbon sulphide in regular octahedrons, melts at 120·5°, and boils at 290°. It takes fire when heated in the air, burning with a reddish flame, and is decomposed by water, with formation of hydriodic and silicic acids. Si_2I_6, obtained by heating the tetra-iodide with finely-divided silver at 280°, crystallises from carbon sulphide in splendid colourless hexagonal prisms or rhombohedrons, which, on exposure to moist air, are converted into a white mass, with formation of silicic and hydriodic acids. When heated, it melts and is reduced to a lower iodide, probably Si_2I_4. Ice-cold water decomposes it, with formation of a white substance, $Si_2O_4H_2$, called *silico-oxalic acid*, from its

analogy to oxalic acid, $C_2O_4H_2$. This body is decomposed, even by weak bases, into hydrogen and silica. $SiHI_3$, formed on passing a mixture of hydrogen and hydriodic acid over silicon heated to low redness, is a colourless strongly refracting liquid, having a density of 3·362 at 0°, and boiling at 220°. It is decomposed by water, like silico-chloroform.

Silicon Tetrafluoride, SiF_4, is a gaseous compound, formed whenever dry hydrofluoric acid comes in contact with silica, either free or combined, and is easily prepared by heating white sand or pounded glass with fluorspar and strong sulphuric acid:

$$2CaF_2 + 2H_2SO_4 + SiO_2 = SiF_4 + 2CaSO_4 + 2H_2O.$$

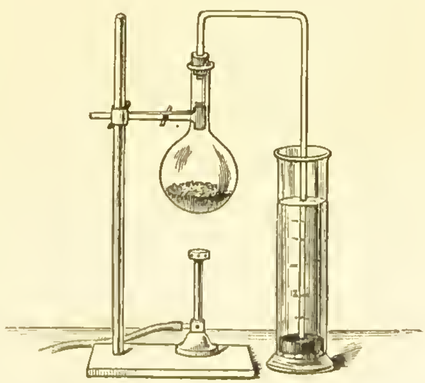
The gas may be collected over mercury. It is colourless, and has a density 3·57 (air = 1), or 52·2 (H = 1). It fumes strongly in the air, has a highly pungent odour, like that of hydrochloric acid, and condenses to a colourless liquid under a pressure of 30 atmospheres, or when cooled to −107°. According to Natterer, it solidifies at −140°. Fused sodium takes fire in the gas, and burns with a red flame. With dry ammonia-gas, it forms a white crystalline compound, $SiF_4,2NH_3$, which is decomposed by water.

Silicofluoric or **Hydrofluosilicic Acid,** H_2SiF_6 or $SiF_4,2HF$, is formed, together with silicic hydroxide or silicic acid, when silicon tetrafluoride comes into contact with water:

$$3SiF_4 + 4H_2O = 2H_2SiF_6 + Si(OH)_4.$$

Experiment.—To prepare it, silicon tetrafluoride obtained as above by heating the materials in a small dry flask, is passed into water through a tube, the lower end of which dips under mercury, as shown in the annexed figure; if the gas were passed immediately into water in the ordinary way, the tube would soon be stopped up by the separated silica.

Fig. 95.



To obtain the acid, the thick jelly is pressed through a linen filter, and the filtrate is concentrated by evaporation in a platinum dish at a low temperature. The saturated solution is a strongly acid fuming liquid, which decomposes on boiling into silicon fluoride and hydrofluoric acid, so that it may be evaporated in platinum, without leaving any residue.

Silicofluoric acid forms salts called *silicofluorides*, having the composition M_2SiF_6 or $M''SiF_6$ (M denoting a univalent and M'' a bivalent metal). Some of these are easily soluble in water, but the potassium, sodium, lithium, barium, and calcium salts are more or less sparingly soluble. By prolonged ignition, they are resolved into silicon fluoride and a metallic fluoride: *e.g.*, $K_2SiF_6 = SiF_4 + 2KF$.

Silicon and Oxygen.

Silicon Dioxide or **Silica**, $(SiO_2)n$, the only oxide of silicon, constitutes, either alone or in combination, a very large proportion of the crust of the earth. It occurs in various forms. Quartz forms crystals, sometimes very large, belonging to the hexagonal system and usually having the form of a hexagonal prism terminated by pyramidal summits (*see* Crystallographic Systems). Density, 2·6. The transparent colourless variety is called rock-crystal. *Amethyst quartz* has a violet tint due to traces of manganese oxides. Other varieties are known as *milk-quartz*, *rose-quartz*, and *smoky quartz*. Sand and sandstone consist of an impure variety.—Tridymite is another hexagonal variety of silica, usually forming six-sided tables having their horizontal edges truncated by pyramidal faces; moreover, the crystals usually occur in twins: hence the name. Density, 2·3.—Amorphous silica occurs as *Opal*, either colourless or variously coloured, and having a density somewhat above 2. It contains water, varying in amount from 0·1 to 12·9 per cent. *Chalcedony*, *agate*, and *flint* are intimate mixtures of amorphous silica with quartz or tridymite.

Hydrated Amorphous Silica is formed as already mentioned (p. 216) by passing silicon tetrafluoride into water. The gelatinous mass washed with water, dried, and ignited, yields pure silica in the form of a white mobile powder.

Experiment.—Amorphous silica may also be prepared by decomposing a silicate of alkali-metal with an acid. Powdered quartz or fine white sand is mixed with about three times its weight of dry sodium carbonate, the mixture is fused in a platinum crucible, and the glassy mass when cold is boiled with water, by which it is softened, and almost entirely dissolved. The liquid is then filtered, an excess of hydrochloric acid is added, and the whole is evaporated to complete dryness. By this treatment the gelatinous silica thrown down by the acid becomes completely insoluble, and remains behind when the dry saline mass is treated with acidulated water, by which the alkaline salts, alumina, ferric oxide, lime, and many other bodies which may happen to be present, are removed. The silica is washed, dried, and heated to redness.

Silica thus prepared is a very fine, white, tasteless powder, having a density of about 2·66, fusible only by the oxyhydrogen blow-pipe. When once dried, it is not sensibly soluble in water or dilute acids, with the exception of hydrofluoric acid. But on adding hydro-

chloric acid to a very dilute solution of potassium silicate, the silica remains in solution, probably in the form of silicic acid. From this mixed solution of silica and potassium chloride, the latter may be separated by diffusion (*see* p. 86), whereby a moderately concentrated solution of silica in water is obtained. This solution has a distinctly acid reaction ; it presents, however, but little stability. When kept for some time, it gelatinises, the silica separating in the insoluble modification. The same effect is produced by the addition of a few drops of sulphuric or nitric acid, or of a solution of salt.

Silica is essentially an acid anhydride, forming salts with basic metallic oxides, and expelling the anhydrides from nearly all salts when heated with them. In strong alkaline liquids it is freely soluble. The majority of silicates are insoluble in water ; the silicates of the alkalis even are not dissolved, unless they contain a relatively large proportion of the alkaline oxide. An alkaline sodium silicate is manufactured under the name of "Soluble Glass." Common glass is a mixture of several silicates, in which the reverse of this happens, the silica being in excess. Glass, however, is slowly acted upon by water.

The molecular weight of silica is unknown, but its non-volatility, high melting-point, and insolubility in water and all solvents, indicate that it probably possesses a somewhat complex structure.

Silicic Acids are unknown, but the solution obtained by diffusion, as just described, may be supposed to contain one of these substances. The composition of known silicates, and the composition and character of the fluoride and chloride of silicon, lead to the inference that orthosilicic acid must be expressed by the formula :

$$H_4SiO_4 \text{ or } 2H_2O.SiO_2.$$

From this compound, by loss of successive portions of water, other acids may be derived thus :

$$2H_4SiO_4 - H_2O = H_6Si_2O_7 \text{ or } 3H_2O.2SiO_2 ;$$

$$2H_4SiO_4 - 2H_2O = H_4Si_2O_6 \text{ or } 2H_2O.2SiO_2 ;$$

$$2H_4SiO_4 - 3H_2O = H_2Si_2O_5 \text{ or } H_2O.2SiO_2.$$

Examples of silicates will be found among the compounds of the metals, especially calcium, magnesium, aluminium, etc. Some of these seem to be derived from formulæ like those given above ; others, however, belong to more complex types, which are very difficult to classify.

Silicon and Sulphur.

Silicon Bisulphide, SiS_2, obtained by passing the vapour of carbon bisulphide over a strongly heated mixture of silica and carbon, such as is used in the preparation of silicon tetrachloride (p. 215), forms long silky needles which are decomposed by water

yielding hydrogen sulphide and silica. The *monosulphide*, SiS, and an *oxysulphide*, probably SiSO, are formed, together with other products, when sulphur-vapour is passed over white-hot silicon. The former is yellow, the latter yellowish, and both are volatile and condense in the cooler, but still hot part of the tube.

Silicon Chlorhydrosulphide, $SiCl_3SH$, is formed by passing a mixture of hydrogen sulphide and vapour of silicon tetrachloride through a red-hot tube: $SiCl_4 + H_2S = HCl + SiCl_3SH$. It is a colourless fuming liquid boiling at 96°. Vapour-density = 5·78 (air = 1).

Silicon and Nitrogen.

A *silicon nitride* of unknown composition is formed by the action of ammonia on the tetrachloride, also when crystallised silicon is strongly heated in nitrogen gas. It is a white amorphous powder insoluble in all acids except hydrofluoric acid, by which it is converted into ammonium silicofluoride. By heating with potash it is converted into ammonia and potassium silicate.

BORON.

Symbol, B. Atomic weight, 11.

This element is not found in nature in the free state, but occurs somewhat abundantly in the form of boric acid, $B(OH)_3$, and some of its salts.

Pure boron is prepared by heating boric oxide, B_2O_3, or potassium borofluoride, with metallic potassium in an iron tube, and washing out the soluble salts with water. As thus obtained, it is a dark brown amorphous powder destitute of taste and smell. It burns in the air when heated, producing the trioxide, and is readily attacked by chlorine, nitric acid, fused alkalis, and other reagents.

Wöhler and Deville, in 1858, by strongly igniting boric oxide with aluminium, in a crucible surrounded with powdered charcoal to prevent access of oxygen, obtained very hard transparent octahedral crystals and a graphite-like substance, which they regarded as modifications of boron analogous to the diamond and graphite varieties of carbon: but subsequent observations have shown that the octahedral crystals contained both carbon and aluminium in the proportions indicated by the formula $B_{48}C_2Al_3$, and that the graphite-like substance was a boride of aluminium having the composition, AlB_2.

Boron Hydride, BH_3, has not been obtained free from excess of hydrogen. A crude magnesium boride is first formed by heating

together boron trioxide and excess of magnesium powder; when this is treated with hydrochloric acid, hydrogen is evolved accompanied by a small quantity of a gas of disagreeable odour. This gas burns with a bright green flame, and is decomposed on passing through a heated tube into boron and hydrogen.

HALOGEN-COMPOUNDS OF BORON.

Boron Chloride, BCl_3, is most readily obtained by passing dry chlorine over a strongly heated mixture of boric oxide and charcoal, whereupon it passes over in vapour, together with gaseous carbon monoxide, and may be condensed to a liquid by passing it through a tube cooled by a freezing mixture. It may be freed from excess of chlorine by agitation with mercury and subsequent distillation. It may also be prepared by heating finely powdered boric oxide with twice its weight of phosphoric chloride for three days in a sealed tube at 150°, and subsequently distilling the product at the temperature of a water-bath. It is a liquid of density 1·35 at 17°, and boiling at 18·23°. It is decomposed by water into hydrochloric and boric acids, and fumes strongly in the air. Heated with sulphuric anhydride in a sealed tube at 120°, it yields boric oxide and sulphuryl chloride: $3SO_3 + 2BCl_3 = B_2O_3 + 3SO_2Cl_2$. It unites with ammonia, forming a white crystalline body, having the composition $2BCl_3,3NH_3$.

Boron Bromide, BBr_3, obtained by direct combination of its elements, or by passing bromine-vapour over a heated mixture of charcoal and boric oxide, is a colourless strongly fuming liquid, having a density of 2·69 and boiling at 90·5. With water and with ammonia it reacts like the chloride.

Boron Fluoride, BF_3, is prepared by heating a mixture of 1 part boric acid and 2 parts fluorspar with 12 parts strong sulphuric acid:

$$2H_3BO_3 + 3CaF_2 + 3H_2SO_4 = 2BF_3 + 3CaSO_4 + 6H_2O;$$

also by heating a mixture of potassium borofluoride and boric oxide with sulphuric acid:

$$6KBF_4 + B_2O_3 + 6H_2SO_4 = 8BF_3 + 6KHSO_4 + 3H_2O.$$

It is a colourless gas, having an extremely pungent odour and a density 2·37 referred to air, or 34·25 referred to hydrogen; it does not attack glass. It is decomposed by water, and must therefore be collected over mercury or by displacement of air.

Potassium and sodium burn brilliantly when heated in it. From many organic substances it withdraws the elements of water, carbonising them at the same time like strong sulphuric acid.

With an equal volume of ammonia it forms the compound BF_3NH_3, which is a white opaque solid, sublimable without altera-

tion. With 2 or 3 volumes of ammonia to 1 volume of BF_3, colourless liquids are formed having respectively the formulæ $BF_3(NH_3)_2$ and $BF_3(NH_3)_3$. These liquids when heated give off ammonia and are converted into the solid compound.

Fluoboric acid, HBF_4, is formed together with boric acid, when boron fluoride is brought in contact with excess of water: $4BF_3 + 3H_2O = 3HBF_4 + B(OH)_3$, also when aqueous hydrofluoric acid is saturated with boric acid. It is a monobasic acid, forming with bases a series of salts called *fluoborides* or *borofluorides*, which are also produced, together with an alkaline hydroxide, or free alkali, on mixing an acid fluoride of potassium or sodium with boric acid: $B(OH)_3 + 2NaHF_2 = NaBF_4 + NaOH + 2H_2O$. This process exhibits the peculiar result of the formation of a liquid having an alkaline reaction by the mixing of two acid liquids. The fluoborides are mostly soluble in water and crystalline. When heated they are resolved into gaseous boron fluoride and a metallic fluoride.

One volume of water absorbs upwards of 1000 volumes of boron fluoride, with great rise of temperature and formation of a fuming oily liquid, which has a density of 1·77, and cauterises like strong sulphuric acid. When heated it gives off about a fifth of the absorbed gas, leaving a liquid which has nearly the composition BF_3,H_2O or $2BF_3,3H_2O$, and boils at 165°–200°, with partial decomposition and formation of boric acid.

The composition of this liquid is very doubtful. It is not improbable that it contains an oxyfluoride associated with hydrogen fluoride, $BF_3 + H_2O = BOF + 2HF$. It seems unlikely that it contains any considerable amount of boric acid, which, on account of its comparatively slight solubility, might be expected to crystallise out.

Boron and Oxygen.—There is but one oxide of boron, viz., the *trioxide* B_2O_3, which unites with water and metallic oxides, forming boric acid and the metallic borates.

Boric or **Boracic Acid**, or **Hydrogen Borate**, $B(OH)_3$ or $3H_2O,B_2O_3$, is found in solution in the hot lagoons of Tuscany, which yield a large supply of it. It is easily prepared by decomposing with sulphuric acid a hot solution of borax, which is a borate of sodium, occurring abundantly in the salt lakes of India, Thibet, and other parts of Asia, also in the United States of America.

Boric acid crystallises in transparent six-sided plates, soluble in about 25 parts of cold water, much more soluble in boiling water. It has but little taste, and differs considerably from the stronger acids in its action on vegetable colours, imparting to blue litmus paper only a wine-red colour, like that produced by carbonic acid, and to turmeric paper a brown colour, like that produced by alkalis, but easily distinguished therefrom by the fact of its not disappearing on the addition of an acid.

The crystallised acid, when heated, gives up its water and melts, with great frothing, to a glassy transparent mass of boric oxide,

which readily dissolves many metallic oxides, with very characteristic colours, *e.g.*, deep blue with oxide of cobalt, amethyst with manganese, bright green with chromium, etc. The crystallised acid dissolves in alcohol, and the solution burns with a green flame.

Glassy boric oxide in a state of fusion requires for its dissipation in vapour a very intense and long-continued heat; the aqueous solution cannot, however, be evaporated without very appreciable loss by volatilisation: hence it is probable that the acid is far more volatile than the anhydrous oxide.

Boric acid is susceptible of modifications analogous to those of phosphoric acid (p. 180), and forming corresponding salts. The acid $B(OH)_3$ or $B_2O_3,3H_2O$, above described, which is analogous in constitution to the chloride, fluoride, etc., of boron, is distinguished as orthoboric acid. This acid, heated at 100°, gives off water, and is reduced to metaboric acid, $B_2O_3.H_2O$ or $BO(OH)$, which is a white powder, volatilising slowly, but completely, at the same temperature. Lastly, when orthoboric acid is heated for a long time at 140°, it gives off more water, leaving pyroboric acid, $2B_2O_3.H_2O$ or $B_4O_5(OH)_2$, in the form of a brittle vitreous mass.

The borates are usually somewhat complicated, owing to the tendency of the normal salts to unite with the elements of boron trioxide or of boric acid. Common borax is represented by the formula $Na_2B_4O_7.10H_2O$. This may be represented as made up of sodium metaborate, $NaBO_2$, with boron trioxide and water of crystallisation, thus:

$$2NaBO_2.B_2O_3 10H_2O.$$

Or it may be regarded as a compound of sodium metaborate, with metaboric acid and water:

$$2(NaBO_2.HBO_2)9H_2O.$$

Lastly, it may be represented as a salt of pyroboric acid, $(HO)_2B_4O_5$.

Boron Trisulphide, B_2S_3, is formed by heating boron in sulphur-vapour, but is more readily prepared by heating an intimate mixture of lamp-black and boric oxide in vapour of carbon bisulphide: $3CS_2+3C+2B_2O_3=2B_2S_3+6CO$. This process yields it for the most part as a white glassy fusible mass, but sometimes in silky needles. It has a pungent odour and attacks the eyes; it melts when heated, and may be distilled in a current of hydrogen sulphide. Water decomposes it immediately, forming boric acid and hydrogen sulphide: $B_2S_3+6H_2O=3H_2S+2B(OH)_3$.

This compound is sometimes supposed to be the source of the boric acid of the Tuscan lagoons, from which hydrogen sulphide commonly escapes.

Boron Nitride, BN or B_3N_3, is produced by heating boric oxide with metallic cyanides, or by heating to bright redness a mixture of sal-ammoniac and pure anhydrous borax, $Na_2O.2B_2O_3$:

$$Na_2O.2B_2O_3 + 2NH_4Cl = 2BN + B_2O_3 + 2NaCl + 4H_2O.$$

It is a white amorphous powder, insoluble in water, infusible and non-volatile. When heated in a current of steam, it yields ammonia and boric oxide : $2BN + 3H_2O = 2NH_3 + B_2O_3$, and likewise gives off a large quantity of ammonia when fused with potash. It dissolves slowly in hydrofluoric acid, forming ammonium fluoborate : $BN + 4HF = (NH_4)BF_4$.

OZONE OR ACTIVE OXYGEN.

It has long been known that dry oxygen or atmospheric air, when exposed to the action of a series of electric sparks, emits a peculiar and somewhat metallic odour, which may also be imparted to moist oxygen by allowing phosphorus to remain in it for some time, and by several other processes. This odorous principle also possesses several properties not exhibited by oxygen in its ordinary state, one of the most characteristic being the liberation of iodine from potassium iodide. It has been the subject of many researches, in the first place by Schönbein of Basle, who believed that common oxygen was capable of assuming two oppositely electrical states, in both of which it exhibited great chemical activity. One of these he called ozone,* the other antozone. Subsequent experiments led to the assumption that ozone consisted of a peroxide of hydrogen. The experiments of Andrews and Tait in 1860, however, showed that ozone was formed by the action of the discharge upon perfectly pure oxygen, and that during the process a contraction of volume occurred. Owing, however, to the impossibility of obtaining ozone apart from a relatively large volume of unchanged oxygen, it was many years before the exact relation of ozone to common oxygen was established. It was, however, finally shown, on the basis of experiments made by Soret in 1865–7, and more especially as the result of elaborate study by Brodie in 1872, that two volumes of ozone consist of the same matter as three volumes of ordinary oxygen ; and hence that the molecule of ozone must be expressed by the formula O_3, when that of oxygen is O_2. There appears to be no second modification of oxygen corresponding to Schönbein's "antozone."

An easy way of preparing ozone is to subject ordinary oxygen to the action of the silent electric discharge. For this purpose a stream of the gas is passed through a tube into which is sealed a pair of very finely-pointed platinum wires with their points at a little distance apart, one being connected with an electrical machine, and the other with the ground. No sparks must be allowed to pass, as in that case a considerable portion of the ozone would be reconverted into ordinary oxygen. A more convenient form of apparatus is provided

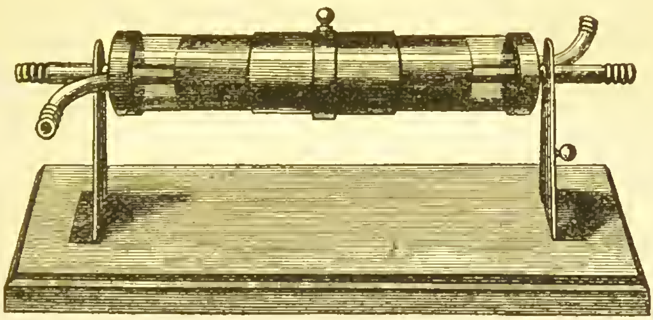
* From ὄζω, to have a smell.

in Siemens' so-called induction tube (fig. 96). This consists of a sort of Leyden-jar, formed of a smooth metal tube which fits into a wider tube coated with tin-foil on its outer surface, leaving a narrow annular space between them. Between the two tubes a stream of pure dry oxygen is passed, which, when the inner and outer coatings are connected with terminal wires of an induction-coil, becomes electrified by induction. By this means from 10 to 15 per cent. of the oxygen may be converted into ozone.

Ozone is also produced in small quantity by suspending a stick of phosphorus in a bottle filled with moist air. It is also formed in the electrolytic decomposition of water, especially when the electrodes consist of short pieces of very thin platinum wire, the proportion of ozone in the liberated oxygen then amounting to nearly one-fifth of its volume. The action of strong sulphuric acid on potassium permanganate also yields ozonised oxygen.

Ozone is but slightly soluble in water and in solutions of acids or alkalis. Air charged with it exerts an irritating action on the lungs.

Fig. 96.



It is decomposed by heat gradually at 100°, instantly at 290°. It is an extremely powerful oxidising agent, possesses strong bleaching and disinfecting powers; corrodes cork, caoutchouc, and other organic substances; oxidises iron, copper, and even silver when moist, as well as dry mercury and iodine. Paper moistened with a mixture of starch and potassium iodide is instantly turned blue when exposed to its action. When paper thus prepared is exposed to the open air for five to ten minutes, it often acquires a blue tint, varying in intensity at different times. Hence it is supposed that ozone is present in the air in variable quantity.

The constitution of ozone has been determined by reference to the following facts:—

1. Ozone exposed to an electric discharge contracts, and the contraction can be measured.

2. Ozone is entirely absorbed by solution of thiosulphate of sodium and by turpentine, and the diminution of volume which results can be measured.

It is found that the contraction which ensues upon electrisation of oxygen is to the subsequent contraction produced by contact of the ozonised gas with the reagent in the ratio of 1 to 2. Hence three volumes of common oxygen produce two volumes of ozone.

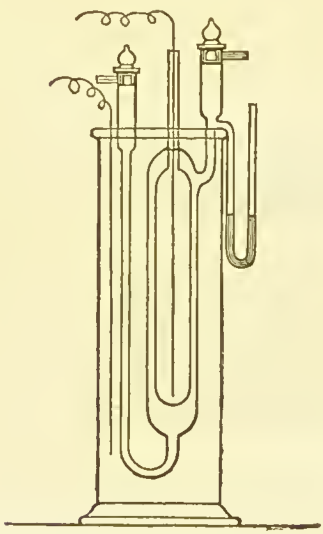
3. When potassium iodide is acted upon by ozone iodine is liberated, but the volume of the gas remains unchanged. This is explained by the following equation which assumes the ratio established by 2 :

$$2KI + O_3 = K_2O + I_2 + O_2.$$

These facts may be demonstrated by the use of the apparatus represented in the accompanying figure 97.

A thin glass tube, open at the top, is sealed into a somewhat wider tube which is provided with an inlet for admission of gas and an exit, which is attached to a U-shaped gauge. The apparatus is immersed in water mixed with ice, the inner tube is filled with dilute sulphuric acid and the gauge is supplied with a short column of strong sulphuric acid, by which any alteration in the volume of the enclosed gas is indicated. Pure oxygen is passed through the apparatus till the air is expelled, the inlet tap is closed, and the level of the sulphuric acid in the gauge marked off. On dipping into the ice water on the outside one of the terminal wires from a Rhumkorff coil, and into the acid water in the inner tube the other terminal, and working the coil, the gas is electrified and contraction is at once indicated by the gauge. If it is desired to bring a reagent, such as turpentine, into contact with the gas, the level of the liquid is observed and the hollow stopper at the top previously charged with a few drops of the liquid is turned so as to allow it to run down into the space occupied by the gas. A further contraction then occurs, which may be measured and compared with the first. If the apparatus is kept immersed in the ice water, the temperature remains constant throughout the experiment.

Fig. 97.



HYDROGEN DIOXIDE.

This compound is formed in a variety of ways, for example, in minute quantity during the combustion of hydrogen in the air, and during the oxidation of several organic substances, such as ether

or turpentine oil, in the presence of air and water. It is, however, always prepared for experimental or practical purposes by decomposition of the peroxide of barium or sodium by an acid :

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2$$

or

$$Na_2O_2 + 2HCl = 2NaCl + H_2O_2.$$

In order to obtain hydrogen dioxide in a pure state, the barium compound is mixed with a little water and gradually added to the acid, taking care that the temperature is not allowed to rise. When a sufficiently strong solution has been obtained, the barium is precipitated by the addition of the requisite quantity of dilute sulphuric acid. This leaves hydrochloric acid in the solution, and to remove it the liquid is shaken up with sufficient silver sulphate, whereby silver chloride is precipitated, and sulphuric acid remains in the liquid. To withdraw the sulphuric acid, pure barium hydrate mixed into a paste with water is gradually added to the liquid, the last portions being precipitated by addition of baryta solution. Throughout all these operations the liquid must be kept at a low temperature. After removing the successive precipitates by filtration, the solution may be concentrated by evaporation over sulphuric acid in a vacuum.

Hydrogen dioxide is a colourless syrupy liquid, which may be concentrated till it attains a specific gravity 1·45. In this state it decomposes very easily, the least rise of temperature causing effervescence, due to the escape of oxygen gas ; near 100° it is decomposed with explosive violence. The dilute aqueous solution is, however, much more stable, and is prepared as an article of commerce. It possesses powerful oxidising and bleaching properties.

Its oxidising action may be exhibited by adding a few drops to a solution of indigo-blue and warming the mixture, when the colour soon disappears. Added to a ferrous salt in the presence of an acid, it converts it into the corresponding ferric salt. A piece of paper smeared with precipitated lead sulphide, PbS (black), is bleached, if wetted with hydrogen dioxide, in consequence of the oxidation of the sulphide to sulphate, $PbSO_4$ (white). Hydrogen dioxide is sometimes used for bleaching hair and for cleaning old oil paintings, the surface of which may have become discoloured by the formation of lead sulphide.

Hydrogen dioxide exhibits a remarkable reaction with certain easily reducible metallic oxides, the metal being reduced, and free oxygen evolved ; *e.g.*, with silver oxide :

$$Ag_2O + H_2O_2 = Ag_2 + H_2O + O_2.$$

It destroys ozone, both substances yielding oxygen :

$$H_2O_2 + O_3 = H_2O + 2O_2.$$

These reactions will be further discussed hereafter.

It also decomposes permanganic acid, and a solution of this compound, acidified with sulphuric acid, forms one of the best tests for the presence of hydrogen dioxide—the disappearance of the purple colour of the liquid and the effervescence due to escaping oxygen being very characteristic :

$$H_2Mn_2O_8 + 2H_2SO_4 + 5H_2O_2 = 2MnSO_4 + 8H_2O + 5O_2.$$

Perhaps the most delicate and characteristic reaction of all is the production of a deep blue compound when added to a solution of chromic acid acidified with sulphuric acid. For the detection of minute quantities of the dioxide, the liquid to be tested should be first shaken with ether, which dissolves the dioxide freely. If this ethereal liquid is then separated from the water and shaken with a few drops of chromic acid acidified with sulphuric acid, the ethereal solution will assume a more or less decided blue colour.

Hydrogen dioxide is a powerful antiseptic and disinfectant, and for the sake of these properties, and for use in bleaching hair and other purposes, considerable quantities are now manufactured in the form of a dilute solution by dissolving sodium peroxide in a slight excess of dilute hydrochloric acid.

It is remarkable that hydrogen peroxide is tolerably stable in the presence of excess of various mineral acids, but undergoes somewhat rapid decomposition when mixed with an alkali.

ARGON.

Symbol, A. Atomic or molecular weight, 39·88. Density, 19·94.

Argon is a colourless, tasteless, inodorous gas, distinguished by its remarkable chemical inertness. It was discovered by Lord Rayleigh and Professor Ramsay in 1894 in atmospheric air, of which it is a constituent to the extent of about 1 per cent. by volume.

Lord Rayleigh's attention was in the first instance attracted by the apparently inexplicable fact that nitrogen gas when derived from atmospheric air was invariably heavier than nitrogen obtained by the decomposition of some chemical compound. A certain globe used in these experiments was found to hold the following quantities of the gas obtained from different sources :—

Chemical Nitrogen.

From Nitric oxide, . . .	2·3001
„ Nitrous oxide, . .	2·2990
„ Ammonium nitrite, .	2·2987

Atmospheric Nitrogen.

Oxygen absorbed by copper, . .	2·3103
„ „ „ iron, . . .	2·3100
„ „ „ ferrous hydrate, .	2·3102

These results correspond to the following weights for 1 litre of the gas :—

Chemical nitrogen, . .	1·2511 gram.
Atmospheric nitrogen, .	1·2572 „

This discrepancy was in the first instance attributed to impurity in the gas from chemical sources ; subsequently it was discovered that the gas supposed to consist wholly of nitrogen, left when the oxygen is withdrawn from air, contains a small quantity of a new gas. It was found by Cavendish, in the middle of the last century, that when air confined over a solution of caustic potash is exposed to the action of a series of electric sparks, the oxygen enters into union with the nitrogen, forming an oxide which is absorbed by the alkali with production of nitrate, and that if additional oxygen is supplied while the sparking is continued, the whole of the gas may be ultimately absorbed with the exception of a small quantity which "we may safely conclude is not more than $\frac{1}{120}$ part of the whole." (Cavendish.)

This residue, which Cavendish was unable to examine further, doubtless consisted chiefly of argon. The sparking process, however, is comparatively slow even with the use of the induction coil, a kind of apparatus which was, of course, unknown to Cavendish. It has been found more convenient to take advantage of the fact that metallic magnesium at a red heat absorbs nitrogen, forming a solid compound, Mg_3N_2. To obtain argon from atmospheric air, therefore, the gas is caused to pass through soda-lime and phosphoric oxide to absorb carbon dioxide and water, then through red-hot spongy copper, whereby the oxygen is removed in the form of solid cupric oxide, and lastly, through a considerable length of tube filled with magnesium powder and heated to bright redness. The removal of the last portions of nitrogen from the residual argon is rather difficult whichever method is adopted.

The density of argon is 19·94. 100 volumes of water dissolve 3·94 vols. of the gas at 12° ; it has therefore nearly the same solubility as oxygen. Argon has been both liquefied and solidified. Its boiling point is $-187°$, and the crystals melt at $-189·6°$. Argon gives two distinct spectra when subjected to the electric discharge under reduced pressure. When the pressure is equal to about 3 mm. of mercury the gas gives a red light, when the pressure is further reduced and the potential of the discharge increased, a blue light is given. Both of these, examined by the spectroscope, exhibit numerous lines, some of which are common to both spectra.

No definite chemical compound has yet been obtained with argon ; it is unchanged by sparking with oxygen in the presence of caustic potash, also by sparking with hydrogen in the presence of acid or of alkali ; it is unaffected by chlorine and even by fluorine and it has no action on sulphur or phosphorus, or metals at a bright red heat. With carbon it seems to combine at the temperature of the electric arc, but the compound has up to the present been scarcely examined

The molecular weight of argon is obtained according to the usual rule, by doubling the number which represents the density of the gas. It is therefore approximately 39·9. But it has been found that argon is probably one of the few known monatomic gases, that is to say, its molecule is composed of one atom only, for on comparing the specific heat of the gas at constant pressure with the specific heat at constant volume, by the method which consists in determining the velocity of sound in the gas, it is found that the ratio is expressed by the value 1·66, which is the same as that found for mercury vapour, which is known to be monatomic. For diatomic gases, such as hydrogen or nitrogen, this ratio is 1·42. The formula for the molecule of argon is therefore A or A_1.

HELIUM.

This name was applied in 1868 by Professors Lockyer and Frankland to a hypothetical element, indicated in the spectrum of the chromosphere by a yellow line of wave length 5875·98, very near to the double lines due to sodium, and since known as D_3. Many years afterwards it was found that certain minerals containing uranium, when dissolved in dilute sulphuric acid, give off a gas which was for a long time supposed to be nitrogen. In 1895, Ramsay discovered that the spectrum of this gas, observed when the light of the electric discharge transmitted through it, under reduced pressure, is viewed by the spectroscope, contains this characteristic line, D_3. The gas, in fact, consists of nitrogen and hydrogen, with a new element, or mixture of elements, which is identical with the previously observed constituent of the sun.

Many minerals have now been found to yield a similar gaseous mixture, either by dissolution in acid or on application of heat. These minerals invariably contain uranium, thorium, or some other heavy metal of high atomic weight, but it is not known which constituent is chiefly concerned in retaining the gas. The gas is not enclosed in cavities, neither is it in the form of ordinary chemical combination, but appears to exist in the mineral in a state of "occlusion," comparable with that condition in which hydrogen is retained by palladium and carbonic oxide by iron. Artificially prepared oxide of uranium does not take up the gas.

Helium is a colourless gas, resembling argon in its inability to form chemical compounds, but its density is little more than one-tenth that of argon, the lowest value yet found being 2·13 (H = 1). The spectrum of helium is characterised by five very brilliant lines, occurring in the red, yellow, blue-green, blue, and violet. D_3 has been found to consist of two lines very close together, and this has been observed in the spectrum of both terrestrial and chromospheric helium. The gas is very slightly soluble in water ; 100 volumes of

water at 18° dissolve ·73 volume of helium. When submitted to fractional diffusion through porous tubes, two portions were separated, having the densities 1·874 and 2·133 respectively; but both specimens gave the same spectra. Very strong evidence, however, would be necessary to establish the possibility of separating light molecules from heavy molecules of the same substance.

Experiments upon the velocity of sound in the gas go to show that helium is, like argon, a monatomic gas, or if it is a mixture, it must be a mixture of monatomic gases. From the density, the molecular weight is approximately 2·13 × 2 or 4·26, but further experiments are necessary in order to determine whether the gas known at present as helium is a single substance or a mixture.

The Bath thermal water has been found to contain a minute quantity of helium; there is, however, none to be detected in atmospheric argon, at any rate, if present, it would represent not more than $\frac{1}{10{,}000}$ part of the air from which it was extracted.

GENERAL LAWS OF CHEMICAL COMBINATION.

Before proceeding further with the study of individual compounds, it is advisable to take a survey of the conditions under which chemical action takes place, and to formulate more precisely than hitherto the quantitative relations observed between substances entering into combination. It is also necessary to recall the fact, of which many illustrations occur in the foregoing pages, that chemical action is always accompanied by evolution or absorption of heat, and frequently by manifestations of electrical action; in fact, that chemical changes are invariably attended by a loss or gain of energy in some form or other in the system of bodies concerned.

I. Conditions essential to Chemical Action.

We will first consider the conditions under which alone chemical action can take place.

1. In order that union may take place between two bodies, or that any chemical interaction may occur between them, they must be in absolute contact. That kind of potential energy which is the cause of chemical combination is usually called *chemical affinity* or *chemical attraction.* Whatever be its true nature, which is at present unknown, it is incapable of operating at any distance appreciable by our senses. In this respect, therefore, it differs from gravitation and the attraction caused by magnetism and by electrical induction.

2. In the second place, chemical combination can take place only within certain limits of temperature. On the one hand, it is found by experiment that cold retards chemical interactions, and that in many cases a sufficient reduction of temperature will put a stop to the formation of combinations which occur readily at a somewhat higher temperature. Phosphorus and iodine, for example, if cooled by a good freezing mixture, may be placed in contact with each other without visible effect. At the common temperature of the air they instantly unite. The absolute zero of temperature ($-273°$ C.) has not yet been attained, but experiments made at about $-180°$ show that all ordinary chemical actions cease at this temperature. Common experience, in respect to the ignition of combustible bodies, points in the same direction. The chemical combinations which occur in burning do not usually begin till the temperature has been raised up to a point which varies in different cases, and depends partly upon the nature of the materials, partly upon their state of division, whether in masses or fine powder, and partly upon their relative masses and the manner in which they are brought together.

On the other hand, while chemical combination can often occur only when a certain elevation of temperature has been reached, there are many cases in which compounds thus formed are destroyed again if the temperature is raised further. For example, many metallic salts combine with water to form crystalline compounds, such, for example, as common alum and the vitriols. This water, however, is somewhat easily driven off by heat. Nitric oxide, again, unites at common temperatures with oxygen, forming the red gas nitric peroxide, but if the temperature is previously raised to about 400°, the two gases remain indifferent to each other.

It is probable that all chemical compounds would be decomposed by heat, if temperatures sufficiently high could be obtained. In some cases the products of the change are capable of reuniting together, if allowed to cool. In such cases the process is spoken of as "dissociation," to distinguish it from those cases of "decomposition," in which the separated elements rearrange themselves into new systems which are incapable of reproducing the original compound on cooling. Thus the effect of heating ammonium chloride is to convert it into a mixture of the two gases, ammonia and hydrogen chloride, which in cooling reunite to form sal-ammoniac. On the other hand, the effect of heat upon ammonium nitrate is to resolve it almost completely into water and nitrous oxide, which do not combine chemically, but retain their independence when cooled.

When one of the substances concerned in the formation of a compound is gaseous at the common temperature, it often happens that pressure alone will promote union without reduction of temperature. The combinations formed by phosphine, PH_3, with the hydracids, hydrogen iodide, bromide, and chloride, afford an example of this effect. Phosphine unites with each of these substances to form a crystalline compound, which, in the case of the iodide, is permanent in dry air at common temperatures. The bromide, however, can be formed only by cooling the mixed gases by a freezing mixture of ice and salt, and the chloride requires a still lower temperature. Combination can, however, be brought about between phosphine and hydrogen chloride by subjecting the mixed gases contained in a glass tube to a pressure of about twenty atmospheres at the temperature of the air (15°–20°). On releasing the pressure, the crystals which have been deposited immediately evaporate off, and the gaseous mixture is reproduced.

II. Conditions which affect the Rate and the Products of Chemical Change.

1. From what has already been stated, it will readily be inferred that elevation of temperature, if properly regulated, will not only initiate chemical action, but will promote its continuance between two bodies.

2. When compounds capable of a mutual exchange of constituents, or what is called "double decomposition," are concerned, other conditions, beside the temperature of the mass, will affect the result to such an extent as often to cause a complete reversal. The best examples will be found among metallic and other salts. When a solution of calcium chloride is mixed with a solution of ammonium bonate / ~~chloride~~, a double decomposition or interchange ensues, and ammonium chloride is left in solution, while calcium carbonate is precipitated:

$$CaCl_2 + (NH_4)_2CO_3 = CaCO_3 + 2NH_4Cl.$$

On the other hand, if calcium carbonate and ammonium chloride, the products of this change, be mixed together in the dry state, and heat is applied, a sublimate of ammonium carbonate is formed, while calcium chloride remains behind.

A similar reversal of a reaction may be obained by changing the liquid solvent in which the interacting bodies are brought together. Potassium carbonate dissolved in water is immediately decomposed by the addition of acetic acid, effervescence ensues from the escape of carbon dioxide and potassium acetate is left in the solution:

$$K_2CO_3 + 2HC_2H_3O_2 = 2KC_2H_3O_2 + H_2O + CO_2.$$

If, however, dry potassium acetate be dissolved in moderately strong alcohol, and carbon dioxide gas is passed into the solution, a white precipitate forms after a time, which is potassium carbonate, while acetic acid passes into solution. The addition of a little water to the mixture will once more afford a medium in which the acetic acid can attack the carbonate, which will dissolve with effervescence due to the liberation of carbon dioxide once more.

In all similar cases, it may be stated that when two salts or compounds capable of double decomposition are mixed together they will begin to interact; but the interaction between them will cease as soon as the change has proceeded to a certain extent, in consequence of mutual action of the products of decomposition upon each other, with reproduction of the original substances. Thus if calcium chloride and potassium nitrate both dissolved in water interact, they produce calcium nitrate and potassium chloride:

$$CaCl_2 + 2KNO_3 = Ca(NO_3)_2 + 2KCl.$$

This process, however, is believed to be limited in consequence of the reproduction of calcium chloride and potassium nitrate:

$$Ca(NO_3)_2 + 2KCl = CaCl_2 + 2KNO_3.$$

Such changes are often spoken of as reversible interactions and are represented symbolically thus:

$$Ca(NO_3)_2 + 2KCl \leftrightarrows CaCl_2 + 2KNO_3.$$

In such cases as this the products remain in the field of action; but when one of the compounds formed is insoluble in the liquid, or is

gaseous at the temperature of the experiment, it is eliminated as fast as it is produced. Consequently the double exchange goes on between successive portions of the materials until one or both are completely consumed and the interaction is complete.

3. Another very important condition which seriously affects many chemical interactions is provided by the "mass" or relative proportions of the acting bodies. A very instructive experiment may be made as follows :—A solution of ferric chloride in water, mixed with a solution of potassium thiocyanate, affords a deep orange-red colour. If a solution is prepared of such a strength that the colour is not too deep to transmit light easily, and to a portion of the liquid a further quantity of ferric salt is added, a deepening of the colour will be noticed, which indicates a further production of the red ferric thiocyanate. From this it would appear that the amount of iron originally added was insufficient to satisfy the equation :

$$6KCNS + Fe_2Cl_6 = 6KCl + Fe_2(CNS)_6.$$

But it will be found that on adding more thiocyanate to another separate portion of the liquid a similar deepening of colour will be visible, which seems to show that there is a deficiency of the thiocyanate. In this case, as in many others, the decomposition of one of the compounds present can never be completely effected unless a very large excess of the other compound which acts upon it is added over and above the quantity requisite according to theory, as expressed in the equation.

Another instance of the action of "mass," complicated to a certain extent by the effects of heat on water vapour, is afforded by the interaction between iron and steam at a red heat. When iron, in the form of nails or borings, is heated to redness in a current of steam, magnetic oxide of iron ($FeO.Fe_2O_3$) is formed and hydrogen liberated from a portion of the steam. On the other hand, oxide of iron, when heated in a tube through which hydrogen is passed, undergoes reduction to the metallic state and water is formed. These apparently inconsistent results are chiefly due to the relative preponderance of steam in the one case and of hydrogen in the other, the excess of steam in the former case carrying off a portion of the liberated hydrogen before it has time to react upon the oxide of iron which has been formed, while in the latter case the hydrogen similarly sweeps away the water vapour before it finds an opportunity of attacking the reduced iron. If the materials were contained in a closed vessel, a state of equilibrium would sooner or later be established, when the amount of water decomposed would be exactly counterbalanced by the amount recomposed in a given time.

4. What is called the *nascent state* is one very favourable to chemical combination. Thus hydrogen *gas* is incapable, under ordinary circumstances, of affecting metallic salts or compounds rich in oxygen like nitric acid. But if in place of the ready-formed gas materials are employed which are capable of producing hydrogen, many changes may be effected which would otherwise be impossible. For example,

if to a mixture of zinc and hydrochloric acid, which is in the act of evolving hydrogen, a small quantity of nitric acid is added, the evolution of gas ceases, and after a short time the nitric acid will be found to have been converted into ammonia.

5. There is yet another obscure class of phenomena, called *catalytic*, in which effects are brought about by the presence of a substance which itself undergoes no perceptible change: the experiment mentioned in the chapter on oxygen, in which that gas is obtained, with the greatest facility, by heating a mixture of potassium chlorate and manganese dioxide, is a case in point. The salt is decomposed at a far lower temperature than would otherwise be required, and yet the manganese oxide is found after the experiment undiminished in amount. It may, however, undergo a temporary alteration. We know, indeed, that this oxide, when in contact with alkalis, is capable of taking up an additional proportion of oxygen and forming a manganate; and it is quite possible that in the reaction just considered it may actually take oxygen from the potassium chlorate, and pass to the state of a higher oxide, which, however, is immediately decomposed, the additional oxygen being evolved, and the dioxide returning to its original state. And in support of this hypothesis it should be mentioned that the oxide of manganese is usually somewhat altered in density and colour, the oxygen which is evolved is accompanied by a small quantity of chlorine, and the residual chloride contains a minute quantity of oxide of potassium. A similar effect in facilitating the decomposition of the chlorate is produced by cupric oxide, ferric oxide, and lead oxide, all of which are known to be susceptible of higher oxidation. The oxides of zinc and magnesium, on the contrary, which do not form higher oxides, are not found to facilitate in the same degree the decomposition of the chlorate; neither is any marked effect produced by mixing the salt with other pulverulent substances, such as pounded glass or pure silica.

The so-called catalytic actions are often mixed up with other effects which are much more intelligible, as the action of finely-divided platinum on certain gaseous mixtures, in which the solid appears to condense the gas upon its greatly extended surface, and thereby to induce combination by bringing the particles within the sphere of their mutual attractions.

III. Laws Relating to Combining Proportions.

1. The Law of Definite Proportions affirms that when two substances unite together to form a given compound they can unite only in a fixed proportion; or, conversely, that any given chemical compound is always composed of the same elements combined in the same proportion.

2. The Law of Multiple Proportions states that the several quantities of any element A which can unite with a fixed quantity of another element B usually stand to one another in simple numerical proportions.

3. The Law of Reciprocal Proportions or Equivalents states that when any two elements, A and B, combine with a third element C, the proportions in which they unite with C are the same in which they unite together, if union occurs between them, or they bear a simple numerical ratio to those proportions. For each element, therefore, there is a fixed proportion in which it enters into any state of chemical union. This quantity is usually called the *chemical equivalent*, and since the equivalent of hydrogen is the smallest known, it is customary to express the equivalents of the other elements in relation to that of hydrogen taken as unity.

The process by which the equivalent of an element is actually determined depends upon circumstances.

a. When a metal dissolves in dilute hydrochloric or sulphuric acid, a weighed quantity of it may be used and the escaping hydrogen carefully measured. From the volume of the gas its weight may be calculated. Thus it is found that 23 parts of sodium, 12 parts of magnesium, or 9 parts of aluminium will displace 1 part by weight of hydrogen. These numbers are the equivalents of the respective metals.

b. Direct combination with hydrogen may be used for the determination of the equivalent. The composition of hydrogen chloride, hydrogen bromide, hydrogen iodide, hydrogen sulphide, and hydrogen oxide or water has been ascertained with great accuracy by processes, some of which have been already indicated (*see* Water, p. 70).

c. If the element is incapable of forming a definite compound with hydrogen, the chloride or some other salt is generally taken for analysis. This is the course adopted with the majority of the metals which for the most part form no compounds with hydrogen, and in the case of such elements as silicon and boron, the compounds of which with hydrogen are gaseous and easily decomposed.

Whatever form of experiment it may be found best to adopt, the object aimed at is the determination of the ratio between the combining quantity of the element in question and that of hydrogen assumed equal to 1, or that of oxygen, chlorine, etc., previously ascertained. The first column of the following table contains the weights of the several elements which are found to combine with or replace 1 part by weight of hydrogen; the second column contains the weights of other elements with which anyone of those on the left is capable of uniting :—

Lithium,	7	Fluorine,	19
Aluminium,	9	Chlorine,	35·4
Magnesium,	12	Bromine,	80
Calcium,	20	Iodine,	127
Sodium,	23	Sulphur,	16
Copper,	31·5	Oxygen,	8
Zinc,	32·5		
Potassium,	39		
Barium,	68·5		

4. Volumetric Combination of Gases. Gases unite by volume in proportions which bear to each other, and to the volume of the resulting compound, a simple numerical relation. This will be evident from inspection of the following examples :—

Gases Uniting.				
1 vol. chlorine	+	1 vol. hydrogen	produce	2 vols. hydrogen chloride.
2 vols. hydrogen	+	1 vol. oxygen	,,	2 vols. water-vapour.
3 vols. hydrogen	+	1 vol. nitrogen	,,	2 vols. ammonia.
2 vols. nitrogen	+	1 vol. oxygen	,,	2 vols. nitrous oxide.
1 vol. nitrogen	+	1 vol. oxygen	,,	2 vols. nitric oxide.
2 vols. carbon monoxide	+	1 vol. oxygen	,,	2 vols. carbon dioxide.
1 vol. mercury-vapour	+	2 vols. chlorine	,,	2 vols. mercuric chloride vapour.

Such facts were discovered by Gay-Lussac, and the above statement is often called Gay-Lussac's Law of Volumes (*see* p. 8).

The Atomic Theory of Dalton.

The general statements of observed fact commonly called *laws* of chemical combination, which have already been enunciated, may be explained by the "Atomic Theory," which, in this application, we owe to John Dalton. According to this theory, the chemical elements are made up of minute indivisible particles or *atoms*, which in each element are all alike in mass and properties, the atoms of hydrogen being, for example, all equal and similar, and different from the atoms of oxygen, which also are all equal and similar. Chemical combination is supposed to result from the close approximation of atoms, either of the same kind or of different kinds, and chemical decomposition is caused by the separation of atoms which were previously united. Hence as the atoms are indivisible, combination can take place only between one, two, three, or more of one kind, with one, two, three, or more of another kind, and so definite, multiple, and reciprocal proportions would be accounted for.

A group of atoms united together chemically is called a molecule.

Physical Constitution of Gases.

In order to explain the properties of gases, of which an account has been given in the earlier pages of this book, a modification and extension of the molecular theory of the constitution of matter has been almost universally adopted by physicists and chemists.

This, which is usually referred to as the Kinetic Theory of Gases, was originally put forward by Joule in 1848, but it was afterwards extended by Krönig and Clausius, and has been further

developed by the investigations and writings of Clerk Maxwell, Lord Kelvin, and other physicists.

According to this theory, it is assumed that the molecules of all bodies are in constant motion; but whereas in solids each molecule oscillates about a fixed centre, from which it never travels very far, the molecules of gases are constantly moving from place to place.

In liquids there is probably an intermediate condition, the molecules moving about, some singly, but the majority in groups of greater or less complexity.

In gases each molecule is supposed to be constantly moving with great velocity in straight lines till it meets another molecule or an impenetrable surface.

As the molecules of a gas are very minute and the number in a given space is, even in greatly attenuated gases, very large, these encounters occur very frequently, and consequently the distance through which each particle can travel in a straight line without interruption, that is, its mean free path, is very small. Some molecules must be assumed to be moving with greater and some with less velocity in consequence of these encounters, but the greater number must be moving with a velocity which approaches to a certain average.

Now the outward pressure against the walls of the containing vessel is, by the hypothesis, the result of the impact of a great number of molecules of gas upon its surface. But at any given temperature, that is, with any given velocity, the number of such impacts taking place in a given time must vary inversely as the volume of the gas; hence the *pressure varies inversely as the volume*, which agrees with the usual statement of Boyle's law.

When a given quantity of a perfect gas is heated it tends to expand by $\frac{1}{273}$ of its bulk at zero for every degree centigrade, and if it is maintained at a constant volume the pressure it exerts upon the walls of the containing vessel increases in the same ratio, that is, proportionally to the absolute temperature.

Now the pressure exercised by the moving molecules upon every unit of area of the surface with which the gas is in contact, is proportional to the sum of the masses of all the molecules (M) multiplied by the squares of their velocities (v^2); and since M remains constant, it is evident that change of pressure is due to change of velocity, and v^2 is therefore a measure of temperature. The law of the expansion of gases by heat is therefore deducible from the kinetic theory.

But the relations between pressure, volume, and temperature of gases, expressed in the laws of Boyle and Gay-Lussac, presuppose certain conditions which, in fact, are never exactly fulfilled. For it must be assumed that the mass of the molecules is infinitely small; and further, that the molecules are entirely independent of each other. It is probable that no gas completely satisfies these conditions, for the known deviations from both laws by the more easily liquefiable gases seem to show that the molecules of such gases are not wholly independent of each other.

On the other hand, it is observed that while in such gases the product of the pressure, P, with the volume of the gas, V, is for moderate pressures less than unity, in the case of hydrogen PV is greater than unity. But when the pressures applied are very great, while the temperature is high enough to prevent liquefaction of the gas, all gases behave like hydrogen. This appears to depend upon the fact that the molecules occupy an appreciable proportion of the whole space filled by the gas, and therefore that each molecule will in the same time strike the walls of the containing vessel more frequently than theory would indicate on the assumption that the molecule was indefinitely small.

The Law of Avogadro, a statement of which will follow immediately, is, of course, subject to limitation similar to that which is applicable to the laws connecting the volume with the pressure and the temperature of a gas. The extent of deviation is illustrated by the case of hydrogen and oxygen, which have been found by the most exact experiments to combine, not exactly in the proportions of 2 vols. : 1 vol., but 2·0024 volumes of hydrogen to 1 volume of oxygen. (Scott.)

The phenomena of the diffusion of gases and the law relating to the rate of diffusion, discovered by Graham (p. 30), are also satisfactorily explained by the kinetic theory. For, assuming that the number of molecules in unit volume of any two gases at the same temperature and pressure is the same (Law of Avogadro), the relative density of each gas will be proportional to its molecular weight. The rate of diffusion of each will depend upon the value of the molecular weight, m, in the expression $\frac{1}{2}mv^2$, which represents the kinetic energy of each. The relative rates of diffusion will therefore be inversely as the square roots of the densities of the two gases.

Law of Avogadro.

All gases have approximately the same coefficient of expansion (see p. 28), and expand and contract to the same extent under the influence of changes of pressure, when the pressure is not so great as to bring the gas near to a change of state. Hence it has been supposed that, as a change of volume must be due to approximation or separation of the particles of the gas, and not to any change in the particles themselves, all gases must be similarly constituted. This hypothesis, formulated in 1811 by Avogadro, and usually referred to as Avogadro's Law, is generally stated thus: *Equal volumes of different gases under like conditions of temperature and pressure contain the same number of molecules.*

By a molecule is here understood a small portion of the substance of the gas made up of atoms which do not separate from one another during the movements of the molecule (*see* Kinetic Theory, p. 239).

This hypothesis is strongly supported by the manner in which gases unite according to Gay-Lussac's Law of Volumes.

Adopting the Law of Avogadro, we can at once understand the nature of the change which occurs when, say, hydrogen combines with chlorine or with oxygen. Whatever measure of hydrogen is taken, it must be assumed to contain n molecules of the gas; then the amount of chlorine, an equal volume, which unites with it must also contain n molecules, and the hydrogen chloride produced, occupying twice the volume of either the hydrogen or the chlorine, must consist of $2n$ molecules of the compound.

Hence it is obvious that each molecule of hydrogen and of chlorine is a double structure, which is divided into two equal parts when combination occurs, one-half of a molecule of hydrogen and one-half of a molecule of chlorine forming a molecule of the compound.

Similarly, when 2 volumes of hydrogen combine with 1 volume of oxygen to form 2 volumes of water in the state of gas, we may state that there are $2n$ molecules of hydrogen, which with n molecules of oxygen form $2n$ molecules of water. Hence the oxygen molecules must be, like those of hydrogen and chlorine, divisible into two equal and similar parts.

Determination of Molecular Weights.

1. The foregoing considerations afford the basis of the most important method for the determination of the relative masses of molecules. The mode of combination of hydrogen, chlorine, and oxygen shows, if Avogadro's hypothesis is true, that one molecule of each of these elements must consist of at least two atoms. If the symbols H, Cl, O be used to represent one atomic proportion of each, then the formulæ of the molecular proportion will be severally H_2, Cl_2, O_2.

Further evidence may be obtained by a consideration of the action of metals upon the hydrogen compounds of chlorine and oxygen, with regard to the manner in which the hydrogen contained in them may be replaced. Compare first hydrogen chloride and water. When hydrogen chloride is acted upon by sodium, *the whole* of the hydrogen is expelled, and the chlorine enters into combination with an equivalent quantity of the metal; thus 36·4 parts hydrogen chloride (=1 part hydrogen+35·4 chlorine) and 23 sodium yield 1 part of free hydrogen and 23 + 35·4 (=58·4) sodium chloride; there is no such thing as the expulsion of part of the hydrogen, or the formation of a compound containing both hydrogen and metal in combination with the chlorine.

With water, however, the case is different. When sodium is thrown upon water, 18 parts of that compound (=2 hydrogen+16 oxygen) are decomposed in such a manner that half of the hydrogen

is expelled by an equivalent quantity of sodium, 23, and sodium hydroxide is formed containing—

Sodium.		Hydrogen.		Oxygen.
23	+	1	+	16

This compound remains in the solid state when the liquid is evaporated to dryness. Water differs, therefore, from hydrochloric acid in this respect, that half its hydrogen may be replaced by sodium, yielding a hydroxide which may be regarded as containing an atom of sodium in place of an atom of hydrogen. The second atom of hydrogen cannot be displaced by the direct action of sodium, but a compound may be obtained by union of sodium and oxygen which must be considered as water, in which both the hydrogen atoms have been replaced by an equivalent quantity of sodium. The relations of the three compounds may thus be represented :

$$\overbrace{\underset{\text{Hydrogen.}}{(1+1)} + \underset{\text{Ox.}}{16}}^{\text{Water.}} \quad \overbrace{(\underset{\text{Hyd.}}{1} + \underset{\text{Sod.}}{23}) + \underset{\text{Ox.}}{16}}^{\text{Sodium hydroxide.}} \quad \overbrace{\underset{\text{Sodium.}}{(23+23)} + \underset{\text{Ox.}}{16}}^{\text{Sodium oxide.}}$$

Or, using symbols to represent the atomic proportions, the relations are displayed still more clearly thus :

$$\underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O} \qquad \underset{\text{Sodium hydroxide.}}{\left.\begin{matrix}H\\Na\end{matrix}\right\}O} \qquad \underset{\text{Sodium oxide.}}{\left.\begin{matrix}Na\\Na\end{matrix}\right\}O.}$$

Now, although water yields up its hydrogen in two stages, the oxygen cannot be displaced except as a whole in one operation. Consequently the oxygen of water is regarded as present in the form of one atom.

If now we write down the quantities of the several elements and compounds under consideration which occupy the same volume in the state of gas, we have the following numbers which represent their relative densities :—

Hydrogen, ...	1
Chlorine, ...	$35\frac{1}{2}$
Oxygen, ...	16
Hydrogen chloride, ...	$18\frac{1}{4}$
Water vapour, ...	9

From considerations already set forth hydrogen chloride consists of

Hydrogen 1 part + Chlorine $35\frac{1}{2}$ parts ;

and if we agree that the atomic weight of hydrogen be taken as unity, the molecule of hydrogen chloride must have the relative weight $36\frac{1}{2}$. Similarly the relative molecular weight of water must be 18. Consequently the molecular weights of vaporisable elements

or compounds are obtained by *doubling the numbers which express their densities in the state of gas.* For the substances already referred to, we therefore arrive at the following statement :—

Names.	Densities or Weights of equal Vols.	Density × 2 or Relative Molecular Weights.	Formulæ representing Molecules.
Hydrogen, . .	1	2	H_2
Chlorine, . . .	$35\frac{1}{2}$	71	Cl_2
Oxygen, . . .	16	32	O_2
Hydrogen chloride, .	$18\frac{1}{4}$	$36\frac{1}{2}$	HCl
Water, . . .	9	18	H_2O

If now this rule is applied to the elements generally, it is found that they differ from one another in molecular complexity as shown in the following table. In some cases, such as iodine and sulphur, it is observed that the relative density is reduced at high temperatures, indicating a simplification of the molecule.

Relative Molecular Density of Vaporisable Elements.

Monatomic.	Diatomic.	Triatomic.	Tetratomic.	Polyatomic.
Hg	H_2	O_3	P_4	S_6 at 500°
Cd	K_2		As_4	
Zn	Cl_2			
I above 1600°	Br_2			
	I_2 below 500°			
	F_2			
	O_2			
	N_2			
	S_2 at 900°			

2. Compounds of carbon with hydrogen, or with hydrogen and oxygen, when exposed to the action of chlorine, frequently exchange a part or the whole of their hydrogen for an equivalent quantity of chlorine, and the number of compounds thus formed affords in some cases a means of determining the molecular weight of the parent compound. For example, marsh gas, or methane, is a compound of 1 part of hydrogen with 3 parts of carbon, or 4 parts of hydrogen with 12 parts of carbon.

When this gas is mixed with chlorine, and exposed to diffuse daylight, a new compound is formed, in which one-fourth of the hydrogen belonging to the marsh-gas is replaced by an equivalent

quantity of chlorine; and if the chlorine is in excess, and the mixture exposed to sunshine, three other compounds are formed, in which one-half, three-fourths, and all the hydrogen are thus replaced. The results may be thus expressed :—

Methane.

$$\overset{\text{Carbon.}}{12} + \overbrace{1 + 1 + 1 + 1}^{\text{Hydrogen.}}$$

Chloromethane.

$$\overset{\text{Carbon.}}{12} + \overbrace{1 + 1 + 1}^{\text{Hydrogen.}} + \overset{\text{Chlorine.}}{35 \cdot 4}$$

Dichloromethane.

$$\overset{\text{Carbon.}}{12} + \overbrace{1 + 1}^{\text{Hydrogen.}} + \overbrace{35 \cdot 4 + 35 \cdot 4}^{\text{Chlorine.}}$$

Trichloromethane or Chloroform.

$$\overset{\text{Carb.}}{12} + \overset{\text{Hyd.}}{1} + \overbrace{35 \cdot 4 + 35 \cdot 4 + 35 \cdot 4}^{\text{Chlorine.}}$$

Tetrachloromethane.

$$\overset{\text{Carbon.}}{12} + \overbrace{35 \cdot 4 + 35 \cdot 4 + 35 \cdot 4 + 35 \cdot 4}^{\text{Chlorine.}}$$

Hence it is inferred, by reasoning similar to that which would be used in the case of the action of sodium on water, that the molecule of marsh gas contains 4 atoms of hydrogen, and hence that its formula and the formulæ of the compounds formed from it by this process of *substitution* must be written in the following manner :—

Methane, ...	$Cx\ H_4$
Chloromethane, ...	$Cx\ H_3Cl$
Dichloromethane, ...	$Cx\ H_2Cl_2$
Trichloromethane, . . .	$Cx\ HCl_3$
Tetrachloromethane, . . .	$Cx\ Cl_4$.

3. When a non-volatile solid, such as sugar or salt, is dissolved in water, the boiling point of the liquid is raised. If quantities of several solids proportional to their molecular weights are added to the same weight of the same liquid, the boiling point is raised to the same extent. This forms the basis of a process for the estimation of the molecular weight in the case of non-volatile compounds, but it is

seldom applied to inorganic acids, or salts, inasmuch as these and other chemically active bodies usually produce a much greater effect than theory would indicate. This is also true of the next process.

4. It has long been known that when a substance of any kind is dissolved in a liquid the temperature must be reduced below the natural freezing point of the liquid before solidification commences, and that even when crystallisation begins the temperature remains below the true freezing point. Researches, chiefly of Professor Raoult, have shown that the depression of the freezing point of a liquid, in which a small quantity of some other substance is dissolved, is proportional to the weight of substance dissolved, and if in different experiments molecular proportions of different substances are used in the same weight of solvent the extent of depression is the same. To determine the molecular weight of a substance the effect upon the freezing point produced by other substances of known molecular weight must be first ascertained. Suppose P the weight in grams of substance dissolved in 100 grams of liquid and C the extent to which the freezing point is lowered. Then $\frac{C}{P}$ is the effect which would be produced by 1 gram; and if M be the molecular weight of the substance, $\frac{MC}{P}$ is the extent to which the freezing point would be lowered by the use of an amount of substance proportional to the molecular weight. Then calling this molecular depression T, the equation

$$\frac{MC}{P} = T$$

affords the means of determining the value of T when M, C, and P are known, or the value of M if T has been previously determined by observation in a number of cases. The liquid used as solvent is usually water, acetic acid, or benzene. For inorganic acids and salts the value of T varies according to the nature of the salt. For carbon compounds and for anhydrous mineral chlorides dissolved in acetic acid or benzene, the following values of T are given :—Water, 19 ; acetic acid, 39 ; benzene, 49. The method is extensively applied to the estimation of the molecular weight of carbon compounds, but there is so much uncertainty still prevailing as to the data for saline compounds that its use in this direction is very limited.

Determination of Atomic Weights.

1. The most obvious and direct method of determining the atomic weight of an element consists in ascertaining the molecular weights

of as many as possible of the compounds into which this element enters and noting the smallest proportion of the element in question ever found in one molecule. The application of this principle will be most readily made intelligible by consideration of a case such as that of oxygen or sulphur.

	Weight of 1 Vol. of Vapour or Relative Density.	Weight of 2 Vols. of Vapour or Molecular Weight.	Weight of Oxygen in 2 Vols.
COMPOUNDS CONTAINING OXYGEN.			
Water,	9	18	16
Carbonic oxide,	14	28	16
Carbonic anhydride,	22	44	32
Nitrous oxide,	22	44	16
Nitric oxide,	15	30	16
Alcohol,	23	46	16
Acetic acid,	30	60	32
Ether,	37	74	16
Etc.,	etc.	etc.	etc.
COMPOUNDS CONTAINING SULPHUR.			Weight of Sulphur in 2 Vols.
Hydrogen sulphide,	17	34	32
Sulphurous anhydride,	32	64	32
Sulphuric anhydride,	40	80	32
Mercaptan,	31	62	32
Carbonic sulphide,	38	76	64
Sulphurous oxychloride,	59½	119	32
Etc.,	etc.	etc.	etc.

On inspection of the last column it is obvious that no compound of oxygen contains in two volumes of vapour, that is in one molecular proportion, less than 16 parts by weight of oxygen. Hence this is taken to be the atomic weight of that element. In like manner 32 is the value indicated for the atomic weight of sulphur.

2. It happens, however, in many cases, notably among the metals, that the element in question yields no compound capable of existing in a state of vapour at a moderate temperature. The determination of the molecular weights of its compounds by the vapour density method is then impossible. Hence for such elements, of which silver and copper are examples, another method must be sought. This is provided by the relation observed between the specific heats

of the elements in the solid state and their atomic weights. Dulong and Petit, in the course of their investigations on specific heat, observed that if the specific capacities for heat of solid elements be computed upon equal weights, numbers are obtained all different, and exhibiting no simple relations amongst themselves ; but if, instead of equal weights, quantities be taken in the proportion of the atomic weights, the resulting specific heats come out very nearly equal, at least in the case of solid and liquid elements, showing that some very intimate connection must exist between the relation of bodies to heat and their chemical nature.

In the following table the solid and liquid elementary bodies are arranged in the order of their specific heats, as determined by

Specific Heats of Elementary Bodies.

Elements.	Specific Heat (that of Water =1).	Atomic Weights.	Product of Sp. Heat × At. Weight.
Lithium, ...	0·9408	7	6·59
Sodium, ...	0·2934	23	6·75
Aluminium, ...	0·2143	27	5·79
Phosphorus { liquid, . .	0·2120	31	6·57
Phosphorus { solid, . .	0·1887	31	5·85
Sulphur, ...	0·2026	32	6·48
Potassium, ...	0·1660	39	6·48
Iron, ...	0·1138	56	6·37
Nickel, ...	0·1080	58	6·27
Cobalt, ...	0·1070	59	6·31
Copper, ...	0·0952	63	6·00
Zinc, ...	0·0956	65	6·21
Arsenic, ...	0·0822	75	6·17
Selenion, ...	0·0762	79	6·02
Bromine (solid), . . .	0·0843	80	6·74
Palladium, ...	0·0593	106	6·28
Silver, ...	0·0570	107·6	6·13
Cadmium	0·0567	112	6·35
Indium, ...	0·0570	113	6·44
Tin, ...	0·0548	117·3	6·43
Antimony, ...	0·0523	120	6·28
Tellurium, ...	0·0475	126	5·98
Iodine, ...	0·0541	127	6·87
Gold, ...	0·0324	197	6·38
Platinum, ...	0·0324	194·3	6·29
Mercury (solid), . . .	0·0319	200	6·38
Thallium, ...	0·0335	204	6·83
Lead, ...	0·0314	207	6·50
Bismuth, ...	0·0308	208	6·40

Regnault, beginning with those whose specific heat is the greatest; and this order, it will be observed, is the inverse of that of the atomic weights in the third column.

A comparison of the numbers in the fourth column of this table shows that, for a considerable number of elementary bodies in the solid state, the specific heats are inversely proportional to the atomic weights, so that the products of the specific heats of the elements into their atomic weights give nearly a constant quantity, the mean value being 6·4. This quantity may be taken to represent the *atomic heat* of the several elements in the solid state, or the quantity of heat which must be imparted to or removed from atomic proportions of the several elements, in order to produce equal variations of temperature.

Carbon, boron, and silicon were formerly regarded as exceptions to this law, their atomic heats, calculated from the specific heats determined at ordinary temperatures, being considerably below the mean value of those of the other elements, as shown by the following table:—

Elements.		Specific Heat.	Atomic Weights.	Product of Sp. Heat × At. Weight.
Boron,		0·2500	11	2·75
Carbon	wood charcoal,	0·2415	12	2·90
	graphite,	0·2008		2·41
	diamond,	0·1469		1·76
Silicon	crystallised,	0·1774	28	4·97
	fused,	0·1750		4·70

F. Weber has, however, shown that the specific heats of these three bodies increase rapidly at higher temperatures, and that at particular temperatures (about 600° for carbon) they become constant, giving for the atomic heats a mean value of about 6, which is nearly the same as that of other elements of small atomic weight, like aluminium and phosphorus, thus:—

	Sp. Heat.	At. Weight.	At. Heat.
Silicon,	0·203	28	5·7
Carbon,	0·467	12	5·6
Boron,	0·5	11	5·5

The metal beryllium is another example of the same anomaly.

The application of this principle to the determination of atomic weights is obvious and simple. The formula

$$\text{Sp.H.} \times \text{At.Wt.} = \text{Constant} = 6{\cdot}4 \text{ Approx.}$$

affords the means of calculating the value of the atomic weight if the specific heat is known. But since the determina-

tion of specific heats is attended by considerable experimental errors, it is not usual to accept the quotient $\frac{6 \cdot 4}{\text{Sp.H.}}$ as the exact value of the atomic weight. The chemical equivalent of the element can usually be determined with great accuracy, and the atomic weight is best found by taking that multiple of the equivalent which approaches most nearly to the value of the quotient $\frac{6 \cdot 4}{\text{Sp.H.}}$

For example, the combining proportion of indium is 37·7, its specific heat ·0570, and the quotient obtained by dividing 6·4 by the specific heat is 112·3. The atomic weight of indium, however, is represented by the number 113·1 or $37 \cdot 7 \times 3$, which is regarded as likely to be nearer to the true value than the number deduced from the specific heat. It is obvious, then, that the use of the law of Dulong and Petit in relation to the valuation of atomic weights is to indicate which multiple of the equivalent ought to be adopted.

3. It was long ago discovered that there is a definite connection between chemical composition and crystalline form. If two compounds contain similar elements, and if from chemical considerations they are supposed to contain the same number of atoms, they frequently crystallise in the same or closely allied forms. Such compounds are said to be *isomorphous* (ἴσος, equal, μορφή, form). The following are examples of groups of isomorphous compounds :—

Magnesium Group of Sulphates.

$MgSO_4 . 7H_2O$
$ZnSO_4 . 7H_2O$
$FeSO_4 . 7H_2O$
$NiSO_4 . 7H_2O$, etc.

The Alums.

$K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$
$K_2SO_4 . Cr_2(SO_4)_3 . 24H_2O$
$K_2SO_4 . Fe_2(SO_4)_3 . 24H_2O$
$(NH_4)_2SO_4 . Al_2(SO_4)_3 . 24H_2O$
$(NH_4)_2SO_4 . Cr_2(SO_4)_3 . 24H_2O$
$(NH_4)_2SO_4 . Fe_2(SO_4)_3 . 24H_2O$, etc.

Phosphates and Arsenates.

$Na_2HPO_4 . 12H_2O$
$Na_2HAsO_4 . 12H_2O$.

$3[Pb_3(PO_4)_2]PbCl_2$ (Pyromorphite)
$3[Pb_3(AsO_4)_2]PbCl_2$ (Mimetisite).

$MgNH_4PO_4 . 6H_2O$
$MgNH_4AsO_4 . 6H_2O$.

Nitrates.	*Sulphates and Selenates.*
$Sr(NO_3)_2$	$MgSO_4 . 7H_2O$
$Ba(NO_3)_2$	$MgSeO_4 . 7H_2O$.
$Pb(NO_3)_2$.	

From these and other examples which might be cited, it appears that one metal may replace another metal, or one non-metal may replace another non-metal, and even that a group of atoms may replace one atom, as NH_4 replaces K, without a change of crystalline form. The term isomorphous is often applied to the elements which thus replace each other, though it does not follow that, when in the elemental state, they would crystallise in the same forms. One of the best indications of isomorphism between two compounds is the capability of crystallising together. A crystal of common alum, immersed in a solution of chrome alum of suitable strength, becomes coated with a purple layer of the latter salt while retaining its octahedral form ; and if solutions of the two alums be mixed, crystals deposited from the mixture contain both aluminium and chromium. Mixtures of isomorphous salts can never be separated by recrystallisation unless they differ greatly in solubility.

Absolute identity of value in the angles of isomorphous substances is not to be expected. The atomic weights and atomic volumes of the contained elements necessarily have an influence, and the unequal effects of heat in causing expansion in the direction of the several axes of the same crystal will tend to produce slight differences. A good example is found in the case of the carbonates of calcium, magnesium, manganese, iron, and zinc, which are found native crystallised in the form of obtuse rhombohedrons (fig. 101, 4), not distinguishable from each other by the eye, but exhibiting small differences in their angles when accurately measured. These compounds are isomorphous, and the measurements of the obtuse angles of their rhombohedrons are as follows :—

Calcium carbonate, ...	105° 5′
Magnesium ,, ...	107° 25′
Manganous ,, ...	106° 51′
Ferrous ,, ...	107°
Zinc ,, ...	107° 40′

Mitscherlich, in 1821, formulated the statement that an equal number of atoms similarly combined produces similarity of crystalline form, and that crystalline form is independent of the chemical nature of the atoms.

This is often referred to as the "Law" of isomorphism. It is, however, in this form much too general, and the converse statement, that similarity of crystalline form indicates similarity of constitution, is also liable to many exceptions. Calcium carbonate, $CaCO_3$, for example, crystallises in rhombohedrons, the same form as sodium nitrate, $NaNO_3$; but although they contain the same number of atoms these salts have undoubtedly a different constitution.

The relations of isomorphism, when observed, may sometimes serve as a clue to the true position of a new element, and hence to a determination of its atomic weight, as, for example, when thallium sulphate is found to yield, by combination with aluminium sulphate, an alum which crystallises with the same amount of water and in the same form as common alum, it is inferred that the amount of thallium which replaces 39 parts by weight of potassium in this compound is the atomic weight of the metal.

4. Atomic weights have been determined in several cases by reference to the Periodic Law. This cannot be conveniently discussed until the relations of atomic volume and valency have been considered.

Specific or Atomic Volume.

The volume occupied by the relative atomic weight of an element in the free state is obtained by dividing the atomic weight by the density. If the element be considered in the gaseous state, it is obvious from what has already been stated (page 243) that the atomic volumes of the known elements in the form of gas will be expressed by the numbers 1, 2, $\frac{1}{2}$, or $\frac{1}{3}$ in different cases.

The most interesting relations are observed among the specific volumes of liquids and solids. The following table exhibits the specific volumes of those solid and liquid elements whose specific gravities have been determined with sufficient accuracy. The elements are arranged in the order of their specific volumes, beginning with the smallest:—

The numbers in the third column of this table do not at first sight exhibit the simplicity of relation which exists between the specific volumes of gaseous bodies. There are, indeed, several causes which contribute to inaccuracy in the observation of the specific gravities or relative densities of these bodies. In the first place, the densities of three of them, viz., mercury, bromine, and chlorine, are such as belong to them in the liquid state, whereas the densities assigned to all the others have been determined in the solid state. In solids, moreover, the density is greatly affected by the state of aggregation, whether crystalline or amorphous, and in dimorphous bodies each form has a density peculiar to itself. Further, as solids and liquids are variously affected by heat, each having a peculiar rate of expansion, and that rate being different at different temperatures, it is not to be expected that their specific volumes should exhibit simple relations, unless they are compared at temperatures at which they are similarly affected by heat. Even gases are found to exhibit abnormal specific volumes if compared at temperatures too near the points at which they pass into the liquid state. In liquids, the simplest relations of specific volume are found at those temperatures for which the tensions of the vapours are equal, that is, at their boiling points; and in solids, the melting points are most probably the comparable temperatures. Now the densities of most of the solid elements in

Specific Volumes of Solid and Liquid Elements.

	Atomic weight.	Relative density.	Specific volume.		Atomic weight.	Relative density.	Specific volume.
Carbon, as *diamond*, .	12	3·52	3·4	Sulphur, *trimetric*, .	32	2·07	15·2
Beryllium, .	9	2·1	4·3	Indium, .	113·4	7·4	15·3
Carbon, as *graphite*, .	12	2·3	5·2	Phosphorus, *red*, . .	31	1·94	15·8
Nickel, . .	58	8·6	6·8	Sulphur, *monoclinic*,	32	1·98	16·2
Manganese, .	54	8·0	6·7	Tin, . . .	117·8	7·3	16
Cobalt, . .	59	8·5	6·9	Selenion, *granular*,	79·0	4·80	16·4
Iron, . . .	56	7·8	7·2	Phosphorus, *yellow*, .	31	1·84	16·8
Copper, . .	63·4	8·95	7·2	Antimony, .	120	6·7	17·9
Chromium, .	52·4	7·01	7·4	Lead, . .	206·4	11·33	18
Iridium, . .	193	21·8	8·8	Selenion, *amorphous*,	79·4	4·28	18·1
Platinum, .	195	21·5	9·10	Tellurium, .	126	6·2	20·3
Zinc, . . .	64·9	7·1	9·1	Bismuth, .	210	9·8	21·2
Palladium, .	106·2	11·8	9·2	Sodium, .	23	0·97	23·7
Rhodium, .	104·1	11·0	9·4	Calcium, .	40	1·58	25
Silver, . .	107·7	10·5	10·2	Iodine, . .	126·5	4·95	25·5
Gold, . . .	196·2	19·34	10·1	Bromine, *liquid*, .	79·75	3·19	25·0
Aluminium, .	27	2·67	10·7	Chlorine, *liquid*, .	35·4	1·33	26·6
Molybdenum,	95·6	8·6	11·1	Strontium, .	87·2	2·54	34·4
Silicon, *graphitoïdal*, .	28	2·5	11·2	Potassium, .	39	0·86	45·6
Lithium, .	7	0·59	11·9	Rubidium, .	85·5	1·52	56·1
Cadmium, .	111·6	8·7	12·9	Cæsium, .	133	1·88	70·6
Uranium, .	240	18·4	13·2				
Arsenic, . .	74·9	5·63	13·3				
Magnesium, .	23·9	1·74	13·8				
Mercury, *liquid*, . .	199·8	14·8	13·5				

the preceding table have been determined at mean temperatures (as at 15·5°), which, in the case of potassium, sodium, phosphorus, and a few others, do not differ greatly from the melting points, but in other cases, as with gold, platinum, iron, &c., are far removed from the melting points. In spite of these causes of inaccuracy, however, the specific volumes of closely related elements are sometimes nearly equal to each other, as, for example, the metals, nickel, manganese, cobalt, iron, copper, chromium. In other cases the atomic volumes of chemically related elements increase as the atomic weight increases. Thus—

Sulphur.	Selenion.	Tellurium
S = 32	Se = 79·4	Te = 126
Sp. vol. 15·2 to 16·2.	16·4 to 18·1	20·3

If the whole of the elements are arranged in the order of the numerical value of their atomic weights a remarkable periodicity is at once apparent.

This is shown in the curve displayed in the plate at the end of the book, originally drawn by the late Professor Lothar Meyer. The curves speak for themselves; it is only necessary to point out that the specific volume does not go on increasing as the atomic weight increases, but reaches a maximum and then falls to a minimum, from which it rises again, and so on, several times in succession. All the known elements range themselves upon or very close to this curve.

Specific Volumes of Solid and Liquid Compounds.—The most general relation that has been observed between the specific volumes of solid compounds, is that *isomorphous compounds have equal specific volumes*, in other words, that their densities are proportional to their molecular weights; such is the case, for example, with the native carbonates of strontium (strontianite) and of lead (cerussite):

Formula.	Molecular weight.	Specific density.	Specific volume.
$SrCO_3$	147·2	3·60	40·4
$PbCO_3$	266·4	6·47	41·2

If the crystalline forms are only approximately similar, the specific volumes also are only approximately equal, the difference being less as the angles of the two crystalline forms are more nearly equal and their axes more nearly in the same ratio. In dimorphous compounds, each modification has a density, and therefore a specific volume, peculiar to itself.

The hydrated sulphates of magnesium, zinc, nickel, cobalt, and iron, which have the general formula, $M''SO_4 + 7H_2O$ (M'' denoting a bivalent metal: see next page), and crystallise in similar forms, have specific volumes very nearly equal to 146; the double sulphates isomorphous with potassio-cupric sulphate, $K_2Cu(SO_4)_2 + 6H_2O$, have specific volumes ranging between 198 and 216; and the alums, *e.g.*, $KAl(SO_4)_2 + 12H_2O$, have specific volumes ranging between 276 and 281.

The specific volume in the liquid state has been studied chiefly with relation to carbon compounds. The most general relation observed is that: *Differences of specific volume are in numerous instances proportional to the differences between the corresponding chemical formulæ.* Thus liquids whose formulæ differ by nCH_2 differ in specific volume by n times 22; for example, methyl formate, $CH_3.CHO_2$, and ethyl butyrate, $C_2H_5.C_4H_7O_2$, which differ by $4CH_2$, have specific volumes differing by nearly 4×22.

Valency or Atomic Value.

We have seen that the atomic weight of an element is in some cases equal to its combining weight, in others, twice, three times, four times, &c., as great; in other words, an atom of certain elements can replace or be substituted for only one atom of hydrogen, whereas the

atoms of other elements can replace 2, 3, 4, &c., atoms of hydrogen. Thus, when sodium dissolves in hydrochloric acid, each atom of sodium replaces 1 atom of hydrogen ; but when zinc dissolves in the same acid, each atom of zinc takes the place of 2 atoms of hydrogen : thus

$$Na + HCl = NaCl + H$$
$$Zn + 2HCl = ZnCl_2 + H_2$$

Here it is seen that an atom of zinc is equal in combining or saturating power to 2 atoms of hydrogen. In like manner, antimony and bismuth form trichlorides, $SbCl_3$ and $BiCl_3$, in which the atom of the metal performs the same chemical functions as 3 atoms of hydrogen, that is to say, it saturates 3 atoms of chlorine ; so also tin in the tetrachloride is equivalent to 4H, and phosphorus in the pentachloride, PCl_5, to 5H.

This difference of combining or saturating power, originally called atomicity, now more appropriately called *valency*, is sometimes denoted by placing dashes or Roman numerals to the right of the symbol of an element, and at the top, as O'', B''', C^{iv}, &c.; and the several elements are designated as—

Univalent	elements, or	Monads,	as H
Bivalent	„	Diads,	„ O''
Trivalent	„	Triads,	„ B'''
Quadrivalent	„	Tetrads,	„ C^{iv}
Quinquivalent	„	Pentads,	„ P^{v}
Sexvalent	„	Hexads,	„ W^{vi}

Elements of even valency, viz., the dyads, tetrads, and hexads, are also included under the general term artiads,* and those of uneven valency, viz., the monads, triads, and pentads, are designated generally as perissads.†

Another method of indicating the replacing values of the elementary atoms, and the manner in which they are satisfied by combination, is to arrange the symbols in diagrams in which each element is connected with others by a number of lines, or connecting bonds, corresponding with its degree of valency ; a monad being connected with other elements by only one such bond, a diad by two, a triad by three, a hexad by six, &c., as in the following examples :—

Water, H_2O . . . . . H—O—H

Carbon dioxide, CO_2 . . . . O=C=O

Ammonium chloride, NH_4Cl . .

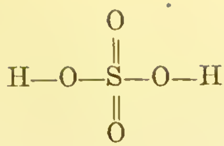
```
    Cl
 H  |  H
  > N <
 H     H
```

Sulphuric oxide, SO_3 . . . .

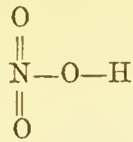
```
 O
 ||
 S=O
 ||
 O
```

* Ἄρτιος, even. † Περισσός, uneven.

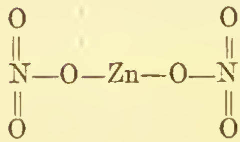
Sulphuric acid, H_2SO_4 . .



Nitric acid, HNO_3 . . . . .



Zinc nitrate, ZnN_2O_6 . .



In most cases, however, these formulæ may be abridged by the use of dots instead of dashes, thus

Water.	Carbon dioxide.	Nitric acid.
H . O . H	O : C : O	O.H over O : $\dot{N}$: O

It must be distinctly understood that these formulæ—which are called *graphic*, *structural*, or *constitutional formulæ*—are not intended to represent the actual arrangement of the atoms in a compound; indeed, even if we had a distinct notion of the manner in which the atoms of any compound are arranged, it could not be adequately represented on a plane surface. The lines connecting the different atoms indicate nothing more than the number of units of valency belonging to the several atoms, and the manner in which they are disposed of by combination with those of other atoms. Thus the formula for nitric acid indicates that two of the three constituent oxygen-atoms are combined with the nitrogen alone, and are assumed to be attached to that element by both their units of valency, whereas the third oxygen atom is combined both with nitrogen and with hydrogen.

By inspection of the preceding diagrams, it will be observed that every atom of a compound has each of its units of valency satisfied by combination with a unit belonging to some other atom. Such, indeed, is the case in every saturated or normal compound. Accordingly it is found that in all such compounds the sum of the perissad elements is always an even number. Thus a compound may contain two, four, six, &c., monad atoms, as ClH, OH_2, CH_4, C_2H_6, C_3H_8, SiH_3Cl; or one triad atom and three monads, as BCl_3; or one pentad and five monads, as NH_4Cl; but never an uneven number of perissad atoms. This is the "law of even numbers," announced some years ago by Gerhardt and Laurent as a result of observation. It was long received with doubt, but has now been confirmed by the analysis of

so many well-defined compounds, that a departure from it is looked upon as a sure indication of incorrect analysis.

For a similar reason, the atoms of elementary bodies rarely exist in the free state, but when separated from any compound, tend to combine with other atoms, either of the same or of some other element. Perissad elements, like hydrogen, chlorine, nitrogen, &c., separate from their compounds in pairs ; their molecule contains two atoms, *e.g.*, H—H. Artiad elements may unite in groups of two, three, or more ; thus the molecule of oxygen, in its ordinary state, probably contains two atoms, that of ozone three atoms ; thus—

Oxygen, ... $O{=}O$

Ozone, ... $\begin{array}{c} O{-}O \\ \diagdown\,\diagup \\ O \end{array}$

The tendency of elementary atoms to separate in groups is shown in various ways. Thus when copper hydride, Cu_2H_2 (to be hereafter described), is decomposed by hydrochloric acid, a quantity of hydrogen is given off equal to twice that which is contained in the hydride itself ; thus—

$$Cu_2H_2 + 2HCl = Cu_2Cl_2 + 2HH.$$

This action is precisely analogous to that of hydrochloric acid on cuprous oxide :

$$Cu_2O + 2HCl = Cu_2Cl_2 + H_2O.$$

In the latter case, the hydrogen separated from the hydrochloric acid unites with oxygen, in the former with hydrogen. Again, when solutions of sulphurous acid and sulphydric acid are mixed, the whole of the sulphur is precipitated :

$$H_2SO_3 + 2H_2S = 3H_2O + SS_2,$$

the action being similar to that of sulphurous acid on selenhydric acid :

$$H_2SO_3 + 2H_2Se = 3H_2O + SSe_2.$$

In the one case, a sulphide of selenion is precipitated ; in the other, a sulphide of sulphur. The precipitation of iodine, which takes place on mixing hydriodic acid with iodic acid, affords a similar instance of the combination of homogeneous atoms :

$$5HI + HIO_3 = 3H_2O + 3II.$$

Another striking illustration of this mode of action is afforded by the reduction of certain metallic oxides by hydrogen dioxide. When silver oxide is thrown into this liquid, water is formed, the silver is reduced to the metallic state, and a quantity of oxygen is evolved equal to twice that which is contained in the silver oxide :

$$Ag_2O + H_2O_2 = H_2O + Ag_2 + OO.$$

Further, elementary bodies frequently act upon others as if their atoms were associated in binary groups. Thus chlorine acting upon

potassium oxide forms two compounds, the chloride and hypochlorite of potassium :

$$ClCl + KKO = KCl + KClO.$$

Again, in the action of chlorine upon many organic compounds, one atom of chlorine removes one atom of hydrogen as hydrogen chloride, while another atom of chlorine takes the place of the hydrogen thus removed. For example, in the formation of chloracetic acid by the action of chlorine on acetic acid :

$$C_2H_4O_2 + ClCl = HCl + C_2H_3ClO_2.$$

Similarly, when metallic sulphides oxidise in the air, both the metal and the sulphur combine with oxygen ; and sulphur acting upon potash forms both a sulphide and a thiosulphate. In all these cases the atoms of the elementary bodies act in pairs.

The number of atoms entering into an elementary molecule, however, varies from one to six or perhaps more (see p. 243).

Variation of Valency.—Multivalent elements often exhibit varying degrees of valency. Thus carbon, which is quadrivalent in marsh-gas, CH_4, and in carbon-dioxide CO_2, is apparently only bivalent in carbon monoxide, CO ; nitrogen, which is quinquivalent in sal-ammoniac, NH_4Cl, and the other ammonium salts, and in nitrogen pentoxide, N_2O_5, is trivalent in ammonia, NH_3 ; sulphur, also, which is apparently sexvalent in sulphur trioxide, SO_3, is quadrivalent in sulphur dioxide, SO_2, and bivalent in hydrogen sulphide, H_2S, and in many metallic sulphides. In these cases, and in others of varying valency, the variation mostly takes place by two units of valency. It is not very easy to account for these variations ; but it is observed in all cases that the compounds in which the valency of a polygenic element is incompletely satisfied tend to pass into a state of saturation, by taking up the required number of univalent or bivalent atoms ; thus carbon monoxide, CO, easily takes up another atom of oxygen to form the dioxide, CO_2, or two atoms of chlorine to form the oxychloride, $COCl_2$; phosphorus trichloride, PCl_3, is readily converted into the pentachloride, PCl_5 ; ammonia, NH_3, unites readily with hydrogen chloride to form sal-ammoniac, NH_4Cl, &c. Similar phenomena are exhibited by many "organo-metallic" bodies, as will be explained further on.

In compounds containing two or more atoms of the same multivalent element, it is supposed one or more units of valency belonging to each of these atoms may be neutralised, by combination with those of another atom of the same kind, so that the element in question will appear to enter into the compound with less than its normal degree of valency. Thus in ethane or dimethyl, C_2H_6, which is a perfectly stable compound, having no tendency to take up an additional number of atoms of hydrogen or any other element, the carbon appears to be trivalent instead of quadrivalent ; similarly in propane, C_3H_8, its valency appears to be reduced to $\frac{8}{3}$; and in butane or diethyl, C_4H_{10} to $\frac{5}{2}$. In all these cases, however, the diminution of

equivalent value in the carbon atoms is only apparent, as may be seen from the following formulæ :

$$\underset{\text{Ethane.}}{\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H{-}C{-}H} \\ | \\ \mathrm{H{-}C{-}H} \\ | \\ \mathrm{H} \end{array}} \qquad \underset{\text{Propane.}}{\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H{-}C{-}H} \\ | \\ \mathrm{H{-}C{-}H} \\ | \\ \mathrm{H{-}C{-}H} \\ | \\ \mathrm{H} \end{array}} \qquad \underset{\text{Butane.}}{\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H{-}C{-}H} \\ | \\ \mathrm{H{-}C{-}H} \\ | \\ \mathrm{H{-}C{-}H} \\ | \\ \mathrm{H{-}C{-}H} \\ | \\ \mathrm{H} \end{array}}$$

or, more shortly, omitting the equivalent marks of the monad atoms :

$$\underset{\text{Ethane.}}{H_3C\,.\,CH_3} \qquad \underset{\text{Propane.}}{H_3C\,.\,CH_2\,.\,CH_3} \qquad \underset{\text{Butane.}}{H_3C\,.\,CH_2\,.\,CH_2\,.\,CH_3}$$

In each of these compounds, every carbon-atom, except the two outside ones, has two of its units of valency satisfied by combination with those of the neighbouring carbon-atoms, while each of the two exterior ones has only one unit thus satisfied. Hence, in any similarly constituted compound containing n carbon-atoms, the number of units of valency remaining to be satisfied by the hydrogen-atoms is $4n-2(n-2)-2=2n+2$. The general formula of this series of hydrocarbons is, therefore, C_nH_{2n+2}, and the equivalent value of the carbon is $\frac{2n+2}{n}$.

In other cases, multivalent atoms may be united by two or more of their units of valency, so that their combining power may appear to be still further reduced, as in the hydrocarbon, C_2H_4, in which the carbon may be apparently bivalent, and in C_2H_2, in which it may appear to be univalent ; thus—

$$\begin{array}{c} \mathrm{H{-}C{-}H} \\ \| \\ \mathrm{H{-}C{-}H} \end{array} \qquad\qquad \begin{array}{l} \mathrm{C{-}H} \\ ||| \\ \mathrm{C{-}H} \end{array}$$

Sometimes also the apparent alteration of combining capacity may be due to the fact that the simplest formula by which a compound may be represented is not its true molecular formula. For example, the two chlorides of tin are usually represented by the formulæ $SnCl_2$ and $SnCl_4$. The second of these is undoubtedly correct, that is to say, the molecule of stannic chloride, as shown by its vapour-density, contains 1 atom of tin and 4 atoms of chlorine, and consequently tin is a tetrad or quadrivalent element. But the lower chloride, in which the tin appears to be only bivalent, has a vapour-density which corresponds closely with the higher formula, Sn_2Cl_4, for this compound, or $Cl_2Sn=SnCl_2$, in which the tin still figures as a tetrad, though relatively to the chlorine it is only bivalent.

Valency is very largely determined by physical conditions, and can only be regarded as limited in respect to the gaseous state. Thus, ammonia represents the limit of the capacity of nitrogen for hydrogen, and hydrogen chloride the limit of the combining power of chlorine for hydrogen in the gaseous state. Nitrogen forms with chlorine very unstable compounds. But ammonia, NH_3, unites with hydrogen chloride, HCl, to form a solid compound, in which it appears that the combining capacity of one or more of the elements present is greater than in ammonia or in hydrogen chloride. This compound, sal-ammoniac, cannot under ordinary conditions exist in a state of vapour, but it may be recrystallised from water, and is able to unite with many other salts, especially with chlorides, forming compounds, of which the following are examples, which, though not vaporisable, have all the characters of definite chemical compounds:—

$$MgCl_2 \;\; 2NH_4Cl$$
$$HgCl_2 \, . \, 2NH_4Cl$$
$$PtCl_4 \, . \, 2NH_4Cl$$

Such compounds as these are often spoken of as "molecular compounds," and are by some chemists regarded as formed by the union of molecules which preserve their integrity within the molecular aggregate, and are held together by something different from ordinary chemical affinity. There is, however, no test by which a "molecular" can be distinguished from an "atomic" combination, and there is evidence that the elements concerned in the formation of the compounds referred to have a greater capacity of combination than is indicated by their vaporisable compounds alone. Water of crystallisation affords another and familiar instance of the formation of compounds which can exist only in the solid or, perhaps, in the liquid state. Such water is united to the salt in definite proportions, and the crystallised compound has properties distinct from those of its constituents, $CuSO_4$, for example, and H_2O are both colourless, but when they unite they form blue vitriol, $CuSO_45H_2O$, which has a different colour, also a definite crystalline form and density which is not related to those of the ingredients. The water in such cases is undoubtedly united to the salt by the oxygen, which is now beginning to be recognised in many other compounds as an element of greater than bivalent capacity. It is evidently quadrivalent, and it may be that, even in carbonic oxide, CO, it is equal in combining capacity to the carbon, which is usually quadrivalent.

The determination of the valency of an element cannot be safely accomplished by reference only to its vaporisable compounds, nor, indeed, by anything short of a complete survey of all its chemical relations. Assistance is very frequently derived from a knowledge of the valency of closely-allied elements; and, in the tabular statement of the Periodic Law, it will be seen that valency is one of the properties which varies periodically with the atomic weight.

Compound Radicles.—Suppose one or more of the component atoms of a fully saturated molecule to be removed: it is clear that the

remaining atom or group of atoms will no longer be saturated, but will have a combining power corresponding with the number of units of valency removed. Such unsaturated groups are called residues or radicles. Methane, CH_4, is a fully saturated compound: but if one of its hydrogen-atoms be removed, the residue CH_3 (called methyl), cannot exist alone but immediately unites with another residue like itself, forming the compound $(CH_3)_2$ or $CH_3 . CH_3$, or it will be ready to combine with one atom of a univalent element, such as chlorine, bromine, &c., forming the compounds CH_3Cl, CH_3Br, &c.; two atoms of it unite in like manner with one atom of oxygen, sulphur, and other bivalent elements, forming the compounds $O''(CH_3)_2$, $S''(CH_3)_2$, &c.; three atoms with nitrogen yielding $N'''(CH_3)_3$, &c.

The removal of two hydrogen-atoms from CH_4 leaves the bivalent radicle CH_2, called methylene, which yields the compounds CH_2Cl_2, CH_2O, CH_2S, &c. The removal of three hydrogen-atoms from CH_4 leaves the trivalent radicle CH, which, in combination with three chlorine-atoms, constitutes chloroform, $CHCl_3$. And, finally, the removal of all four hydrogen-atoms from CH_4 leaves the quadrivalent radicle carbon capable of forming the compounds CCl_4, CS_2, &c.

In like manner, *ammonia*, NH_3, in which the nitrogen is trivalent, yields, by removal of one hydrogen-atom, the univalent radicle amidogen, NH_2, which, with one atom of potassium, forms potassamine, NH_2K, and when combined with one atom of the univalent radicle methyl, CH_3, forms methylamine, $NH_2(CH_3)$, &c. The abstraction of two hydrogen-atoms from the molecule NH_3, leaves the bivalent radicle imidogen, NH, which with two methyl-atoms form dimethylamine, $NH(CH_3)_2$, &c.; and the removal of all three hydrogen-atoms from NH_3, leaves nitrogen itself, which frequently acts as a trivalent element or radicle, forming tripotassamine, NK_3, trimethylamine, $N(CH_3)_2$, &c.

Finally, the molecule of *water*, OH_2, by losing an atom of hydrogen, is converted into the univalent radicle hydroxyl, OH, which, in its relations to other bodies, is analogous to chlorine, bromine, and iodine, and may be substituted in combination for one atom of hydrogen or other monads. Thus, water itself may be regarded as H.OH, analogous to hydrogen chloride, HCl; potassium hydroxide as K.OH, analogous to potassium chloride; barium hydroxide, as $Ba(OH)_2$, analogous to barium chloride, $BaCl_2$.

From the preceding explanations of the mode of derivation of compound radicles, it is clear that there is no limit to the number of them which may be assumed; in fact, it is only necessary to suppose a number of units of valency abstracted from the formula of any saturated molecule, in order to obtain a radicle of corresponding combining power or equivalent value. But unless a residue is found to enter into a considerable number of compounds, thus forming them into a group, like the salts of the same metal, there is nothing gained by conferring upon it a name.

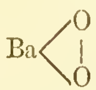
It must also be distinctly understood that these compound radicles are mere formulæ and do not usually represent anything which can exist in the separate state. Thus hydroxyl—O—H is not known in the free state, the actually existing compound containing the same proportions of hydrogen and oxygen being O_2H_2 or H—O—O—H. In like manner methyl, CH_3, has no separate existence, but dimethyl, C_2H_6, is a known compound :—

Methyl.	Dimethyl.
$—CH_3$	$CH_3 . CH_3$

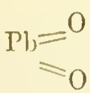
From what has been stated it appears that elements possessing more than one unit of valency may enter into combination in such a way as to link together two or more atoms or groups of atoms into a chain, which in some cases may be shown to extend to almost indefinite length, especially among the compounds of carbon (p. 258).

The study of the "constitution" of compounds on the assumption of this theory of the linking of atoms now forms an important part of the business of scientific chemistry. The greatest advances have been made in the chemistry of carbon compounds, usually denominated "Organic Chemistry," but, even among inorganic compounds, it is possible to obtain a certain amount of evidence of definite arrangement or order among the component elements. One or two examples will serve to indicate the general nature of the process.

Lead peroxide and barium peroxide have the same empirical formula, that is, they are both represented as dioxides, PbO_2 and BaO_2. The question arises whether the oxygen is attached to the metal in the same way in the two compounds. If lead peroxide is dissolved in hydrochloric acid an unstable lead perchloride, $PbCl_4$, is produced together with water ; while, if barium peroxide is dissolved in hydrochloric acid, barium chloride is formed and hydrogen dioxide. This last compound is always represented as H—O—O—H, because, with the valency which hydrogen and oxygen atoms are respectively believed to possess, no other arrangement is possible. Hence the oxygen in barium dioxide is supposed to be in a similar condition, and the formula becomes



in which the metal takes the place of the two atoms of hydrogen. In lead peroxide, on the other hand, there is no reason to suppose that the oxygen atoms are united, and the formula is written

 or $O{=}Pb{=}O$.

Sulphuric acid, H_2SO_4, is a bibasic acid ; that is, it exchanges the half or the whole of its hydrogen for metals, giving an acid or a neutral salt ; sodium sulphates for example,

$$NaHSO_4 \quad \text{and} \quad Na_2SO_4 .$$

Both atoms of hydrogen, therefore, appear to be in the same condition.

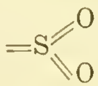
If sulphuric acid is treated with pentachloride of phosphorus it yields a compound, $HClSO_3$, which, when mixed with water, regenerates sulphuric acid with hydrogen chloride. Evidently

$$H_2SO_4 - HO + Cl = HClSO_3 .$$

If this compound, $HClSO_3$, is heated alone it yields sulphuric acid and a volatile compound, SO_2Cl_2. Here again

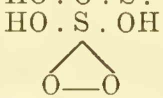
$$HClSO_3 - HO + Cl = SO_2Cl_2 .$$

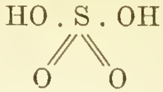
Sulphuric acid is therefore resolvable into $HO + HO + SO_2$. It may be reproduced from these materials ; that is, by the action of hydrogen dioxide upon sulphur dioxide. Hydrogen dioxide, acting upon sulphites, also produces sulphates ; and sodium dioxide unites with sulphur dioxide with vivid incandescence, $Na_2O_2 + SO_2 = Na_2SO_4$. As to the group, SO_2, there is no direct evidence to indicate the arrangement of these atoms, but from its analogy with chromium, and for other reasons, sulphur is commonly regarded as hexad, and if this view is accepted, the formula becomes



The highest chloride sulphur is known to form is SCl_4, and that is unstable. Hence it is evident that we are not able to assign a complete constitutional formula to sulphuric acid, as the choice lies between the three expressions

I. HO . O . S . O . OH . . (S bivalent)

II.  . . . (S quadrivalent)

III.  . . . (S sexvalent)

It is safest to write it $(HO)_2(SO_2)''$. Disulphuric or pyrosulphuric acid would then be written $HO.SO_2.O.SO_2.OH$.

When sulphur is added to a sulphite a new salt is produced, which was formerly improperly called sodium hyposulphite (q.v.), though now more appropriately termed a thiosulphate, since it contains the elements of a sulphate in which one atom of oxygen is replaced by one atom of sulphur. Inspection of the formula of the sulphate shows that the oxygen exists in the molecule in two positions, (1) either wholly attached to sulphur, or (2) linking the metal to the sulphur ; and the point is to determine which of these two positions is taken up by the entering sulphur. The facts seem to accord best with the assumption that the sulphur occupies the

latter position. For when a thiosulphate is mixed with an acid, sulphur is deposited and sulphur dioxide set free; and silver and lead thiosulphates, when heated, give the sulphides of these metals. The formula of thiosulphuric acid is therefore usually written

$$HS \,.\, SO_2 \,.\, OH.$$

Another instructive instance is afforded by acetic acid, $C_2H_4O_2$. This is a monobasic acid, the formulæ of the salts of sodium and silver being $C_2H_3NaO_2$ and $C_2H_3AgO_2$ respectively. When acted upon by phosphorus pentachloride, an exchange of HO for Cl occurs, as in the case of sulphuric acid, resulting in the formation of a chloride, C_2H_3OCl. This is a volatile compound, which is immediately decomposed by water, with reproduction of acetic acid and formation of hydrogen chloride—

$$C_2H_3OCl + HHO = C_2H_3O \,.\, OH + HCl.$$

Evidence as to the atomic arrangement within the group, C_2H_3O, is afforded by the action of chlorine and by the action of alkali upon an acetate at a high temperature. When acetic acid is attacked by chlorine three out of the four atoms of hydrogen may be ultimately replaced by chlorine, the product being a monobasic acid like acetic acid. Thus

Acetates.	Trichloracetates.
$HC_2H_3O_2$	$HC_2Cl_3O_2$
$NaC_2H_3O_2$	$NaC_2Cl_3O_2$
$KC_2H_3O_2$	$KC_2Cl_3O_2$
$AgC_2H_3O_2$	$AgC_2Cl_3O_2$

The fourth atom of hydrogen in acetic acid is not replaceable by chlorine, but only by metals; hence it seems evident that the latter is in a state of combination different from the former. Now, it has been shown that one atom of hydrogen is intimately associated with oxygen, and the other three atoms are, therefore, probably attached to carbon. This is proved by the result of heating an acetate with caustic potash, whereby the carbon is divided into two parts, one half going to form a carbonate, the other half escaping with hydrogen in the form of marsh-gas.

This is symbolised in the following way:—

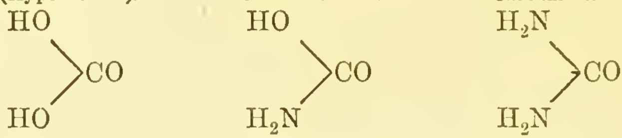
$$\begin{array}{ccccccc}
\text{Acetate.} & & \begin{array}{c}\text{Caustic}\\ \text{Potash.}\end{array} & & \text{Marsh-Gas.} & & \begin{array}{c}\text{Potassium}\\ \text{Carbonate.}\end{array} \\
\begin{array}{r} CH_3 \\ | \\ KO \,.\, CO \end{array} & + & \begin{array}{c} H \\ \\ OK \end{array} & = & \begin{array}{c} CH_4 \\ \\ \\ \end{array} & + & \begin{array}{c} \\ \\ KO \,.\, CO \,.\, OK \end{array}
\end{array}$$

That the carbonate has the constitution here ascribed to it seems to be proved by many facts. Thus, carbon monoxide, CO, unites with two atoms of chlorine to form the compound $COCl_2$, which interacts with water in the same way as the chlorides already mentioned as derived from sulphuric and acetic acids; that is to say, it exchanges Cl for HO, producing the acid. And, although in this case the acid

cannot be obtained in a solid or pure liquid state apart from a large excess of water, carbonic acid is represented by a large class of stable salts, the carbonates, about which there is no difference of opinion.

Carbonic acid is also capable of conversion into and reproduction from two amides, which are both well recognised compounds. The relations between them are shown as follows :—

Carbonic Acid. (Hypothetical). Carbamic Acid. Carbamide.



By such processes and such considerations the chemist endeavours to decipher the problems presented by chemical compounds of which the composition has been determined. In some cases assistance may be derived from a knowledge of the physical properties, such as boiling point, density, or refractive power ; but such methods are at present applicable almost exclusively to the study of carbon compounds, and can only be used in connection with a pretty extensive knowledge of "organic" chemistry.

CLASSIFICATION.

The classification of substances which come under the notice of the chemist may be in the first instance based on their composition ; that is, they may be divided into *compound* and *simple* bodies or elements. So far as inorganic materials are concerned, the most numerous and important substances are metallic oxides and salts. These will be referred to later.

As to the elements, the division into Metallic and Non-Metallic has already (Introduction) been referred to, and has been practically acted upon in the arrangement of the subject-matter of this book. It remains to be stated what are the characteristics of each class.

The popular idea of a metal as something hard, heavy, and having a peculiar lustre, is of course useless for scientific purposes, inasmuch as many well-known metals, such as sodium, potassium, and aluminium, are comparatively light, while there are many substances of high specific gravity and specular lustre which, like galena, iodine, and graphite, are certainly not metals. The distinguishing characters of the metals as a class are summed up by saying that they are elements which form the best conductors of heat and electricity, they are malleable and ductile, they form with hydrogen few compounds, and those never gaseous or even vaporisable ; and their oxides, if not too rich in oxygen, interact with acids to form salts and water. Further, in the electrolysis of their compounds they appear at the negative electrode or cathode, and are commonly referred to as electro-positive elements.

Non-metals, on the other hand, when solid, are feeble conductors, brittle, and combine with hydrogen to form gaseous compounds, while their oxides, with very few exceptions, such as nitric oxide and carbonic oxide, are acid anhydrides, combining with water to form acids, and with metallic oxides to form salts. In the electrolysis of acids or salts the non-metals are liberated at the positive electrode or anode. The non-metals are therefore regarded as electro-negative.

It is, however, impossible to bring all the known elements under these two heads, for some, like arsenic and antimony, while preserving the aspect and high density of common metals and forming many well-defined salts, yet give also strongly acidifying oxides, and form gaseous compounds with hydrogen. For such imperfect metals as these the name Metalloid seems most appropriate.

Another system of classification would be based upon the valency or atom-fixing power. This, however, would be insufficient without taking other considerations into account, as it would bring together such incongruous substances as sodium and chlorine, boron and gold. Similar remarks apply to a division of the elements according to their isomorphous relations, though in this case it will be noticed that the isomorphous groups include usually only those elements which, for other reasons, would be associated together, and seem really to constitute a natural family. The following table gives a synopsis of the more important families of isomorphous elements according to the definition given, p. 250 :—

Isomorphous Groups.

(1)	(3)	(6)
Sulphur	Iron (ferric)	Lithium
Selenion	Manganese (ic)	Silver
Tellurium	Chromium	Thallium
	Aluminium	Gold
		Sodium
		Potassium
(2)		Rubidium
Magnesium	(4)	Cæsium
Calcium	Barium	
Manganese (ous)	Strontium	(7)
Iron (ferrous)	Lead	Fluorine
Cobalt		Chlorine
Nickel		Bromine
Zinc		Iodine
Cadmium	(5)	
Copper	Tin	(8)
	Titanium	Phosphorus
	Zirconium	Arsenic
		Antimony
		Bismuth
		Vanadium

All these different considerations are now merged in a comprehensive scheme usually referred to as the Periodic Law. It was first pointed out by Newlands in 1864 that if the elements be ranged in order, according to the numerical value of their atomic weights, at every eighth term of such a series an element is found which presents a revival or repetition of the same characters starting from any point in the series. So that, as the atomic weight increases, there is not a continuous modification of characters, but a *periodic* rising and falling of valency and other chemical as well as physical characteristics. At the time that this periodicity of properties was first observed, the scheme was necessarily very imperfect, owing to the fact that the atomic weights of many elements, especially metals, were as yet unfixed by appeal to the specific heat or otherwise. Many important details of this scheme were afterwards worked out by Odling, Lothar Meyer, and Mendelejeff.

Arranging the elements in horizontal lines according to this order, as in the following table (in which the atomic weights are, for the most part, represented by their nearest whole numbers), we find that, with the exception of certain metals belonging to the iron and platinum groups, they stand in such a manner that the first vertical column is occupied by the monad elements, the second by the diads, the third by the triads, &c., as indicated by the headings of the columns in which the symbol R stands for a metal or a non-metal. Hydrogen stands alone, there being no known element intermediate between it and the monad metal lithium, if we except the newly-discovered gas, helium, of supposed atomic weight 4·0, but concerning the true nature of which much remains to be learned.

The elements in each of the first six groups of this table range themselves naturally in two columns, each composed of elements closely related to one another in their chemical properties; thus in Group I., the left-hand column contains the alkali metals, lithium, sodium, while the right-hand column includes the metals potassium, rubidium, and cæsium, which, though very closely related to the former two, are sharply distinguished by the characters of their salts. Similarly, in Group II., calcium is nearly related to magnesium, and formerly the oxides of these two metals were ranked together as alkaline earths, but magnesium and its compounds are more truly regarded as the forerunners in a series in which zinc and cadmium follow. Again, in Group VI., the first column is formed by the closely related non-metallic elements, oxygen, sulphur, selenion, and tellurium; while the second contains the metals chromium, molybdenum, tungsten, and uranium, which also greatly resemble one another in their chemical relations, and which are connected with the sulphur groups, not only by valency, but by the isomorphism of chromates with sulphates, and the general resemblance of the oxide CrO_3 to SO_3, and of the oxychloride, CrO_2Cl_2 to SO_2Cl_2, and in other ways.

The elements in Group III., column 1, boron, aluminium, gallium, indium, and thallium, are undoubtedly triads. Aluminium

forms a trichloride, $AlCl_3$, and a corresponding oxide, Al_2O_3 ; also a volatile methyl-compound, $Al(CH_3)_3$, the vapour density of which indicates that the molecule, as represented by this formula, has the normal 2-volume condensation. It is true that the chloride, which is also volatile, exhibits up to 400°–500° a vapour-density agreeing rather with the double formula, Al_2Cl_6, but at 800°–900° the vapour-density agrees with the formula $AlCl_3$, and it is therefore probable that the lower temperature at which its vapour-density was determined was not sufficiently raised above the boiling point to bring the compound into the state of a perfect gas.

The rare earth metals in Group III., column 2, have been shown to be triads, forming trichlorides and sesquioxides. All the elements in Group IV. have long been classed as tetrads, with the exception of cerium, the valency of which was regarded as doubtful ; but the experiments of Brauner seem to have shown that it is a tetrad.

Of the elements in Group V., phosphorus, antimony, niobium, and tantalum form pentachlorides. Nitrogen is assumed to be quinquivalent in the ammonium-compounds, as in the chloride NH_4Cl. Vanadium, arsenic, and bismuth do not combine with more than three atoms of chlorine, bromine, or iodine ; but bismuth forms an oxychloride, $BiOCl_3$, in which it is quinquivalent, and vanadium forms the analogous compound, $VOCl_3$. Arsenic does not form a similar oxychloride ; but its highest oxide is the exact analogue of phosphoric oxide and vanadic oxide, and forms a series of salts, the arsenates, which are isomorphous with the phosphates and vanadates, and these are best expressed on the assumption that the central element is quinquivalent. For these reasons arsenic is likewise regarded as a pentad.

Among the elements in Group VI., chromium, molybdenum, tungsten and uranium form oxychlorides, MO_2Cl_2, and trioxides, MO_3. Sulphur, selenion, and tellurium, so far as regards their hydrogen compounds, H_2S, &c., are diads ; but with regard to their combinations with chlorine, they are tetrads, and sulphur is known to form certain organic compounds in which it is tetradic, and others in which it is hexadic, for example :—

$$\text{Sulphur triethiodide, } S^{iv}\left\{\begin{matrix}(C_2H_5)_3\\ I\end{matrix}\right.$$

$$\text{Sulphur diethylene-dibromide, } S^{vi}\left\{\begin{matrix}(C_2H_4)''\\ (C_2H_4)''\\ Br_2\end{matrix}\right.$$

Moreover, the chemical relations of the sulphates are much more clearly represented by formulæ in which sulphur is supposed to be hexadic, like that given for sulphuric acid on p. 262, than by formulæ into which it enters as a diad, such as, H—O—O—S—O—O—H, inasmuch as compounds in which diadic elements are linked together in one row, may be supposed to be less stable, like the higher oxides and sulphides of potassium. These three elements are therefore best

	Group I.		II.		III.		IV.		V.		VI.		VII.		VIII.
Series.	Monads. R_2O.		Diads. RO.		Triads. R_2O_3.		Tetrads. RH_4. RO_2.		Triads or Pentads. RH_3. R_2O_5.		Diads or Hexads. RH_2. RO_3.		Monads or Triads. RH.		Various.
1	H. 1														
2	Li 7		Be 9	—	B 11	—	C 12	—	N 14	—	O 16	—	F 19		
3	Na 23		Mg 24		Al 27	—	Si 28	—	P 31	—	S 32	—	Cl 35·4		
4	—	K 39	—	Ca 40	—	Se 44	—	Ti 48	—	V 51	—	Cr 52	—	—	{ Fe 56 { Ni 58 Cu 63 { Mn 54 { Co 59
5	—	—	Zn 65	—	Ga 69	—	Ge 72		As 75	—	Se 79	—	Br 80	—	
6	—	Rb 85	—	Sr 87	—	Y 89	—	Zr 90	—	Nb 94	—	Mo 96	—	—	{ Ru 102 { Pd Ag 108 { Rh 103 { 106
7	—	—	Cd 112	—	In 113	—	Sn 118	—	Sb 120	—	Te 126 ?	—	I 127	—	
8	—	Cs 133	—	Ba 137	—	La 133	—	Ce 141		Di 146 ?	—	—	—	—	
9	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
10	—	—	—	—	—	—	—	—	—	Ta 182	—	W 184	—	—	{ Ir 193 { Pt Au 197 { Os 191 { 195
11	—	—	Hg 200	—	Tl 204	—	Pb 207		Bi 210	—	—	—			
12	—	—	—	—	—	—		Th 234				U 239			

regarded as hexads, though they sometimes enter into combination as tetrads, and very frequently as diads.

Oxygen, in its combinations with hydrogen, and with most of the metals, is apparently bivalent; but it appears also to be capable of higher degrees of combination; for water is certainly not to be regarded as a saturated compound, inasmuch as it exhibits capacity for very diverse forms of combination, not only with metallic salts, but with large numbers of carbon compounds. From its analogies to sulphur, and the place of its atomic weight in the series, it may, perhaps, be classed with the hexads, though there is usually no evidence of greater combining capacity than four units.

Of the remaining elements, manganese appears to stand toward chlorine in much the same kind of relationship as chromium does to sulphur or vanadium to phosphorus. It is, however, so much more nearly allied to iron that it is properly associated with that element, which, for the present, must be relegated to the extra Group VIII.

Several permanganates are said to be isomorphous with the corresponding perchlorates; but, on the other hand, the manganates are isomorphous with the chromates and sulphates, and many manganous and manganic salts are isomorphous with the corresponding compounds of iron. Too much importance must not be attached in this case to the relations indicated by isomorphism alone.

The four oxyacids of chlorine form a regular series, so far as empirical formula is concerned, inasmuch as they contain a regularly increasing quantity of oxygen; and if it be assumed, as sometimes is done, that chlorine is capable in its more complex compounds of exercising a combining capacity equal to seven units, the formula of these acids may be represented in the following manner in which the valence of the chlorine varies by two units, from 1 to 7; thus—

$$\mathrm{Cl{-}O{-}H} \qquad \mathrm{O{=}Cl{-}O{-}H} \qquad \mathrm{O{=}}\overset{\overset{\displaystyle O}{\|}}{\mathrm{Cl}}\mathrm{{-}O{-}H} \qquad \mathrm{O{=}}\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{\mathrm{Cl}}}\mathrm{{-}O{-}H}$$

Hypochlorous. Chlorous. Chloric. Perchloric.

When, however, the great difference in properties between chloric and the far more stable perchloric acid is considered, it seems improbable that their structure is so nearly the same as suggested by these formulæ. The unstable chloric acid is more likely to be built up on the same plan as the hypochlorous and chloric acids, and this would not involve the assumption of a higher valency than three units for chlorine, which more nearly assorts with what is known of its behaviour in other combinations. The formula for chloric acid would then be $\mathrm{O{=}Cl{-}O{-}O{-}H}$ or $\mathrm{Cl{-}O{-}O{-}O{-}H}$. On the other hand, perchloric acid is by the same assumption as to the maximum combining capacity for chlorine reduced to the formula

$$\mathrm{H{-}O{-}Cl}\left\langle\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\rangle\mathrm{O}.$$

Among carbon compounds greater stability is in many cases associated with the formation of a closed chain, and it may be that a similar connection exists in the compounds of other elements. The investigation of this question is, however, far more difficult.

Turning now to the compounds of manganese, we find no evidence that it ever exhibits a valency expressed by an uneven number. At the most it is hexad. On this hypothesis the manganates are represented by a formula corresponding to the accepted formula for the sulphates, namely :—

$$\begin{array}{ccc} KO\diagdown & & \diagup\!\!\!\diagup O \\ & Mn & \\ KO\diagup & & \diagdown\!\!\!\diagdown O \end{array}$$

and the permanganates by a formula derived from this, probably as follows :—

$$\begin{array}{ccccc} & OK & & OK & \\ O\diagdown\!\!\!\diagdown & | & & | & \diagup\!\!\!\diagup O \\ & Mn & O\text{—}O\text{—} & Mn & \\ O\diagup\!\!\!\diagup & & & & \diagdown\!\!\!\diagdown O \end{array}$$

From these the corresponding expressions for the oxides MnO_3 and Mn_2O_7 are easily deduced.

Iodic acid, IO_3H, and periodic acid, IO_4H, are perhaps similar in constitution to chloric and perchloric acids, and the anhydride, I_2O_5, is also known. Bromic acid, BrO_3H, is similar to chloric acid, but the existence of perbromic acid is doubtful. Of fluorine no oxygen-compound is known; but from the close analogy in the reactions of these four elements, Cl, Br, I, and F, and the manner in which they replace one another in combination, there can be no doubt that they belong to the same group. In their combinations with hydrogen, and in the reactions in which they replace hydrogen and one another in combination, they invariably act as monads, the substitution taking place atom for atom.

Fluorine, like the other three, shows signs of a greater capacity for combination in the production of a considerable number of well-defined double compounds, such, for example, as the fluorides of hydrogen and potassium and of hydrogen and silicon.

$$KHF_2 \text{ or } K.F{=}F.H \qquad H_2SiF_6 \text{ or } HF\Big\langle \begin{array}{c} F \\ | \\ F \end{array} \Big\rangle Si \Big\langle \begin{array}{c} F \\ | \\ F \end{array} \Big\rangle FH$$

There is no occasion to attribute to fluorine a higher valency than three.

Lastly, with regard to the elements (all metallic) which cannot be included in either of the seven groups above considered. The atomic weights of three of these metals, viz., iron, cobalt, and nickel, have values between those of manganese and copper; and of the other six, called p l a t i n u m m e t a l s, three, viz., ruthenium, rhodium, and

palladium, have atomic weights intermediate between those of molybdenum (96) and silver (108), while those of the other three, viz., osmium, iridium, and platinum, are greater than that of tungsten and nearly equal to that of gold.

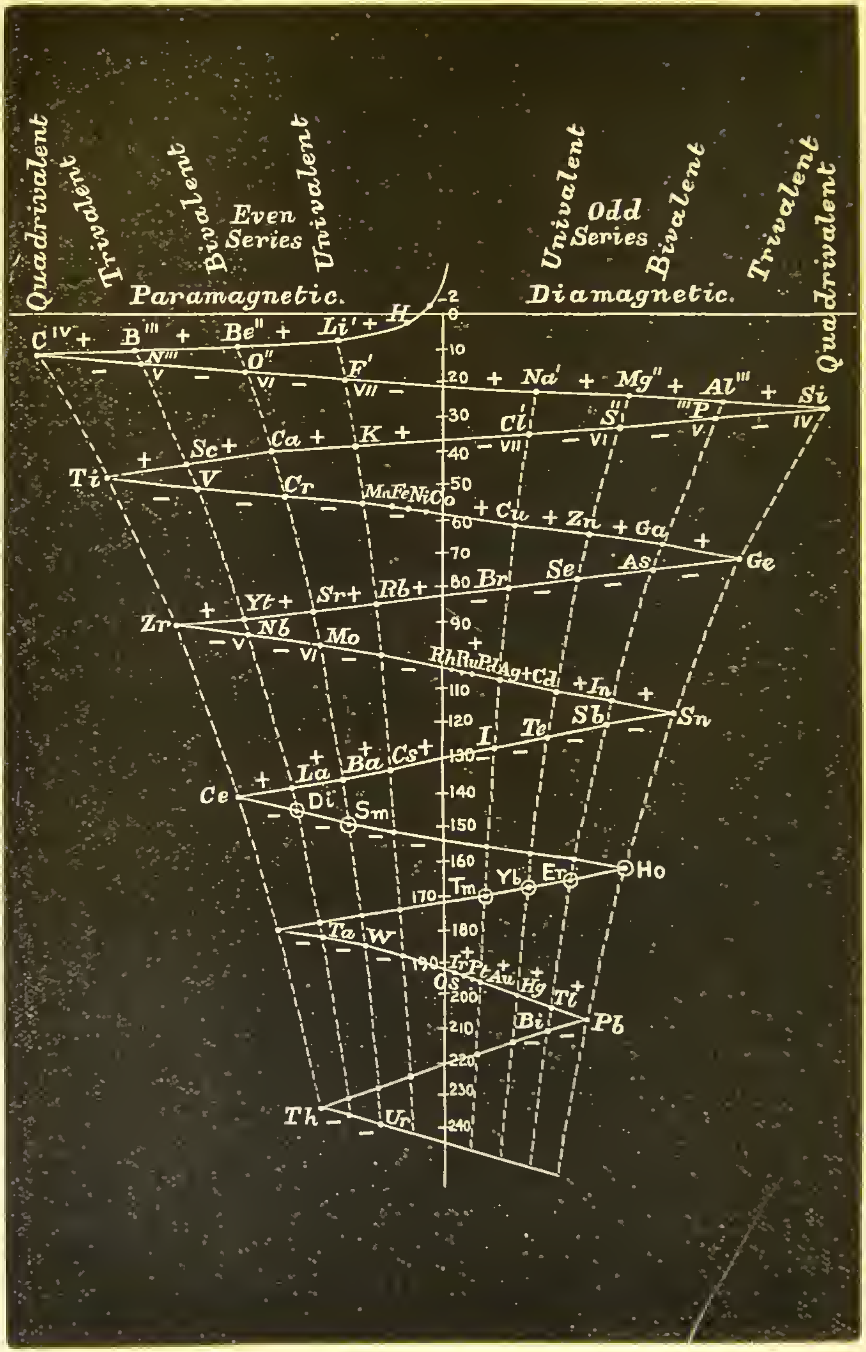
These intermediate elements, Mn, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, constitute a group of themselves (the eighth), some of the members of which, viz., Ru and Os, form tetroxides, the constitution of which is still unknown. None of these metals form chlorides containing more than four atoms of chlorine, but four of them, viz., Pt, Ir, Ru, and Os, form with the alkali-metals double chlorides, the constitution of which is probably similar to that of other double chlorides and to the double fluorides already referred to.

The blank spaces in the preceding table indicate the places of elements which perhaps exist, but have not yet been discovered. Several anticipated discoveries of this kind have, however, been actually realised. When the table was drawn up, a blank in the space now occupied by gallium indicated the probable existence of a trivalent element intermediate in atomic weight between zinc and arsenic. This element was provisionally designated *Ekaluminium* by Mendelejeff, who predicted, from its position in the series, what its chief properties ought to be. The discovery of gallium with the atomic weight 68·8 has verified this prediction. Another example is afforded by scandium, which agrees closely in properties and atomic weight (44) with the element whose existence was predicted by Mendelejeff under the name of *Ekabor*.

A still more recent example is afforded by the element Germanium, discovered in 1886, which belongs to the tetrads along with silicon and tin.

Various plans have been proposed for displaying graphically the relations which have thus been discovered. A diagram devised by Professor Emerson Reynolds, and subsequently modified by Mr Crookes, is shown on page 272. In this form the periodic recurrence of the same type is shown by an oscillating curve, the amplitude of the swing gradually declining according to a mathematical law. It has been used to illustrate the idea that the so-called elements may have been evolved by successive condensations of a primordial material, probably as a consequence of cooling from a high temperature above that at which the constituents of all ordinary matter may be supposed to be dissociated.

Fig. 98.


Quadrivalent
Trivalent
Bivalent
Even Series
Univalent
Paramagnetic.
Univalent
Odd Series
Bivalent
Trivalent
Quadrivalent
Diamagnetic.

CRYSTALLISATION ; CRYSTALLINE FORM.

ALMOST every substance, simple or compound, capable of existing in the solid state, assumes, under favourable circumstances, a distinct geometrical figure, usually bounded by plane surfaces, and having angles of constant value. The faculty of crystallisation seems to be denied only to a few bodies, chiefly highly complex organic principles, which stand, as it were, upon the very verge of organisation, and which, when in the solid state, are frequently characterised by a kind of beady or globular appearance, well known to microscopical observers.

The most beautiful examples of crystallisation are to be found among natural minerals, the results of exceedingly slow changes constantly occurring within the earth. It is invariably found that artificial crystals of salts, and other soluble substances which have been slowly and quietly deposited, surpass in size and regularity those of more rapid formation.

Solution in water or some other liquid is a very frequent method of effecting crystallisation. If the substance be more soluble at a high than at a low temperature, then a hot and saturated solution left to cool slowly will generally be found to furnish crystals : this is a very common case with salts and various organic principles. If it be equally soluble, or nearly so, at all temperatures, then slow spontaneous evaporation in the air, or over a surface of oil of vitriol, often proves very effective.

Fusion and slow cooling may be employed in many cases : that of sulphur is a good example : the metals, when thus treated, usually afford traces of crystalline figure, which sometimes become very beautiful and distinct, as with bismuth. A third condition under which crystals very often form is in passing from the gaseous to the solid state, in the process usually called "sublimation," of which iodine affords a good instance. When by any of these means time is allowed for the symmetrical arrangement of the particles of matter at the moment of solidification, crystals are produced.

That crystals owe their figure to a certain regularity of internal structure is shown both by their mode of formation and also by the peculiarities attending their fracture. A crystal placed in a slowly-evaporating saturated solution of the same substance, grows or increases by a continued deposition of fresh matter upon its sides, in such a manner that the angles formed by the meeting of the latter remain unaltered.

The tendency of most crystals to split in particular directions, called *cleavage*, is a certain indication of regular structure, while the optical properties of many among them, and their mode of expansion by heat, point to the same conclusion.

It may be laid down as a general rule that every substance has its own crystalline form, by which it may very frequently be recognised

at once—not that each substance has a different figure, although very great diversity in this respect is to be found. Some forms are much more common than others, as the cube and six-sided prism, which are very frequently assumed by a number of bodies not in any way related.

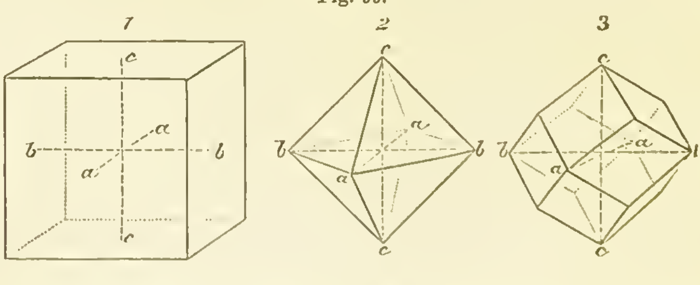
The same substance may assume, under different sets of circumstances, as at high and low temperatures, two different crystalline forms, in which case it is said to be *dimorphous*. Sulphur and carbon furnish, as already noticed, examples of this curious fact; another case is presented by calcium carbonate in the two modifications of calcspar and arragonite, both chemically the same, but physically different. A fourth example is presented by mercuric iodide, which also has two distinct forms, and even two distinct colours, the contrast between the two modifications being indeed as great as that between diamond and graphite.

When two substances having a similar chemical constitution crystallise in the same forms so as to replace each other exactly in crystallised compounds, without altering the geometrical figure, they are said to be *isomorphous*. This has already been explained, and examples supplied in connection with the question of the choice of atomic weights (pp. 249–251).

Crystallographic Systems.—When a crystal of simple form is attentively considered, it becomes evident that certain directions can be pointed out in which straight lines may be imagined to be drawn, passing through the central point of the crystal from side to side, from end to end, or from one angle to that opposed to it, &c., about which lines the particles of matter composing the crystal may be conceived to be symmetrically built up. Such lines, or *axes*, are not always purely imaginary, however, as may be inferred from the remarkable optical properties of many crystals: upon their number, relative lengths, position, and inclination to each other, depends the outward figure of the crystal itself.

All crystalline forms may upon this plan be arranged in the following six classes or systems.

Fig. 99.

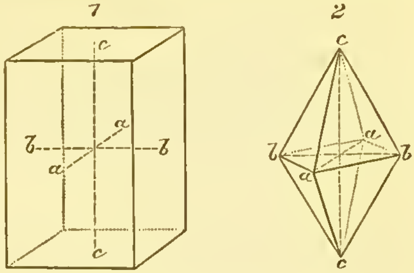


1. **The monometric, regular, or cubic system** (fig. 99).—The crystals of this division have three equal axes, all placed at right angles to each other. The most important forms are the *cube* (1), *the regular octahedron* (2), and the *rhombic dodecahedron* (3).

The letters *a—a*, *b—b*, *c—c* (fig. 99), show the termination of the three axes, placed as stated.

Very many substances, both simple and compound, assume these forms, as most of the metals, carbon in the state of diamond, common salt, potassium iodide, the alums, fluor-spar, iron bi-sulphide, garnet, spinelle, &c.

Fig. 100.

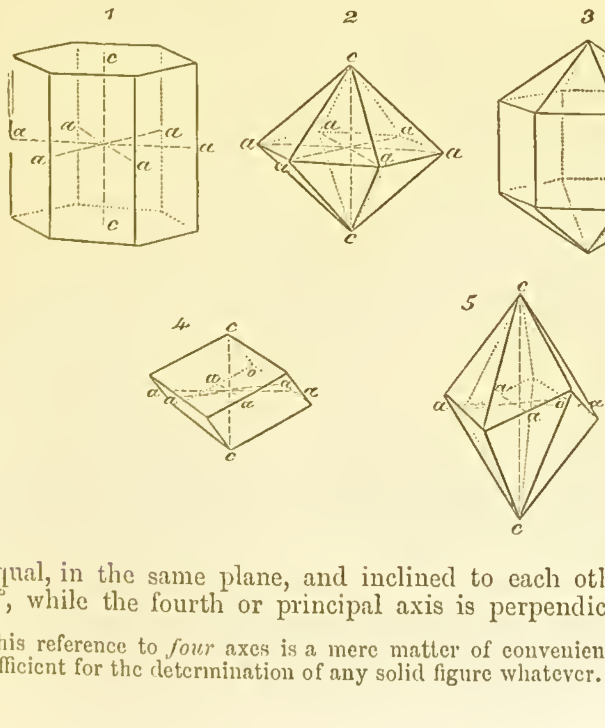


2. The dimetric, quadratic, or tetragonal.—The crystals of this system (fig. 100) are also symmetrical about three axes at right angles to each other. Of these, however, two only are of equal length, the third, *c—c*, being longer or shorter. The most important forms are, the *right square prism* (1), and the *right square-based octahedron* (2).

Examples of these forms are to be found in zircon, native stannic oxide, apophyllite, potassium ferrocyanide, &c.

3. The hexagonal system (fig. 101).—This is very important and extensive; it may be characterised by *four* axes,* three of which

Fig. 101.



are equal, in the same plane, and inclined to each other at angles of 60°, while the fourth or principal axis is perpendicular to them

* This reference to *four* axes is a mere matter of convenience; *three* axes are sufficient for the determination of any solid figure whatever.

all. The principal forms are,—the *regular six-sided prism* (1), the *regular double six-sided pyramid* (2), the *rhombohedron* (4), and the *scalenohedron* (5), a figure bounded by twelve scalene triangles.

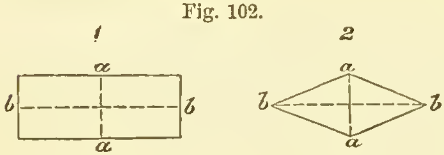
Examples are found in ice, calcspar, sodium nitrate, beryl, quartz or rock-crystal, and the semi-metals, arsenic, antimony, and tellurium.

A combination of the regular six-sided prism and double six-sided pyramid (3) is a common form of quartz.

4. **The trimetric, orthorhombic, or right prismatic system.** —This is characterised by three axes of unequal lengths, placed at right angles to each other, as in the *right rectangular prism*, the *right rhombic prism*, the *right rectangular-based octahedron*, and the *right rhombic-based octahedron.*

The bases of these forms are represented in fig. 102 (1) and (2). Let the reader imagine a straight line passing through the centre of each of these figures, perpendicular to the plane of the paper; this will represent the vertical axis. The octahedrons will be formed by joining the ends of this vertical line with the angles of the bases, and the prisms by vertical planes passing through the sides of the base, and terminated by horizontal planes passing through the extremities of the vertical axis. The perspective forms of these trimetric prisms and octahedrons are similar to those of the dimetric system (fig. 100).

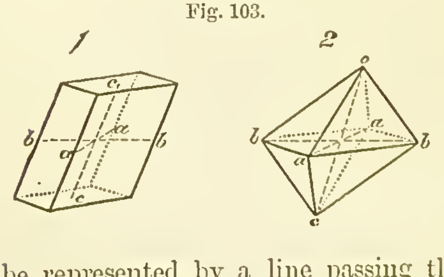
Fig. 102.



The system is exemplified in sulphur crystallised at a low temperature, arsenical iron pyrites, potassium nitrate and sulphate, barium sulphate, &c.

5. **The monoclinic, or oblique prismatic system.** Crystals belonging to this group have also three axes, which may be all unequal; two of these (the secondary) are placed at right angles, the third being so inclined as to be oblique to one and perpendicular to the other. To this system may be referred the four following forms:—*The oblique rectangular prism*, the *oblique rhombic prism*, the *oblique rectangular-based octahedron*, the *oblique rhombic-based octahedron.*

Fig. 103.



The bases of these monoclinic forms are identical in form with those of the trimetric system, fig. 103 (1) and (2). The principal axis may be represented by a line passing through the plane of the paper at the middle point, perpendicular to *a a*, and oblique to *b b*. The perspective forms are shown in fig. 103.

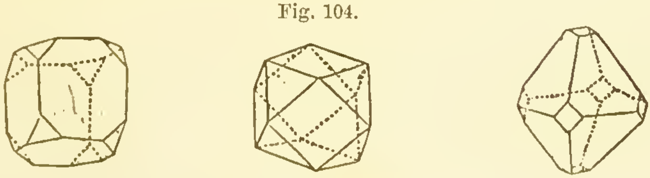
Such forms are taken by sulphur crystallised by fusion and cooling, by realgar, sulphate, carbonate and phosphate of sodium, borax, green vitriol, and many other salts.

6. **The triclinic, anorthic, or doubly oblique prismatic system.**—The crystalline forms comprehended in this division are, from their great apparent irregularity, exceedingly difficulty to study and understand. In them are traced three axes, which may be all unequal in length, and are all oblique to each other, as in the *doubly-oblique prism*, and in the *doubly-oblique-octahedron.* The perspective forms are similar to those of the monoclinic system.

Copper sulphate, bismuth nitrate, and potassium quadroxalate afford illustrations of these forms.

Primary and Secondary Forms.—If a crystal increase in magnitude by equal additions on every part, it is quite clear that its figure must remain unaltered ; but if, from some cause, this increase should be partial, the newly-deposited matter being distributed unequally but still in obedience to certain definite laws, then alterations of form are produced, giving rise to figures which have a direct geometrical connection with that from which they are derived. If, for example, in the cube, a regular omission of successive rows of particles of matter in a certain order be made at each solid angle, while the crystal continues to increase elsewhere, the result will be the production of small triangular planes, which, as the process advances, gradually usurp the whole of the surface of the crystal, and convert the cube into an octahedron. The new planes are called *secondary*, and their production is said to take place by regular *decrements* upon the solid angles. The same thing may happen on the edges of the cube; a new figure, the rhombic dodecahedron, is then generated. The modifications which can thus be produced of the original or

Fig. 104.



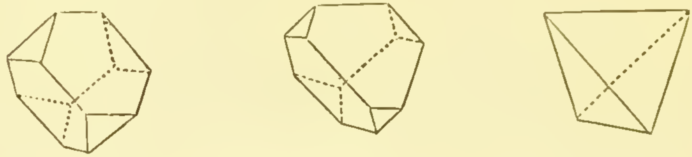
Passage of cube to octohedron.

primary figure (all of which are subject to exact geometrical laws) are very numerous. Several distinct modifications may be present at the same time, and thus render the form exceedingly complex.

Crystals often cleave parallel to all the planes of the primary figure, as in calcspar, which offers a good illustration of this perfect cleavage. Sometimes one or two of these planes have a kind of preference over the rest in this respect, the crystal splitting readily in these directions only.

A very curious modification of the figure sometimes occurs by the excessive growth of each alternate plane of the crystal; the rest become at length obliterated, and the crystal assumes the character called *hemihedral* or *half-sided.* This is well seen in the production of the tetrahedron from the regular octahedron (fig. 105), and of the

Fig. 105.



Passage of octohedron to tetrahedron.

rhombohedric form by a similar change from the double six-sided pyramid (fig. 101, 2).

Forms belonging to the same crystallographic system are related to each other by several natural affinities.

1. *It is only the simple forms of the same system that can combine into a complex form.*—In all fully-developed (holohedral) natural crystals, it is found that all the similar parts, if modified at all, are modified in an exactly similar manner, while in hemihedral forms, half the similar edges and angles alternately situated are similarly modified. Now this can be the case only when the dominant form and the modifying form are developed according to the same law of symmetry. Thus, if a cube and a regular octahedron are developed round the same system of axes, each summit of the cube is cut off to the same extent by a face of the octahedron, or *vice versa.* But a cube could never combine in this manner with a rhombic octahedron, because it would be impossible to place the two forms in such a manner that similar parts of the one should throughout replace similar parts of the other.

The crystals of each system are thus subject to a peculiar and distinct set of modifications, the observation of which very frequently constitutes an excellent guide to the discovery of the primary form itself.

2. *Crystals belonging to the same system are intimately related in their optical properties.*—Crystals belonging to the regular system (as the diamond, alum, rock-salt, &c.) refract light in the same manner as uncrystallised bodies; that is to say, they have but one refractive index, and a ray of light passing through them in any direction is refracted singly. But all other crystals refract doubly, that is to say, a ray of light passing through them (except in certain directions) is split into two rays, the one, called the *ordinary* ray, being refracted as it would be by an amorphous body, the other, called the *extraordinary* ray, being refracted according to peculiar and more complex laws. Now the crystals of the dimetric and hexagonal systems resemble each other in this respect, that in all of them

there is one direction, called the optic axis, or axis of double refraction (coinciding with the principal crystallographic axis), along which a ray of light is refracted singly, while in all other directions it is refracted doubly ; whereas in crystals belonging to the other systems, viz., the trimetric and the two oblique systems, there are always *two* directions or axes, along which a ray is singly refracted.

3. *Crystals belonging to the same system resemble each other in their mode of conducting heat.*—Amorphous bodies and crystals of the regular system conduct heat equally in all directions, so that, supposing a centre of heat to exist within such a body, the isothermal surfaces will be spheres. But crystals of the dimetric and hexagonal systems conduct equally only in directions perpendicular to the principal axis, so that in such crystals the isothermal surfaces are ellipsoids of revolution round that axis ; and crystals belonging to either of the three other systems conduct unequally in all directions, so that in them the isothermal surfaces are ellipsoids with three unequal axes.

ALLOTROPY AND ISOMERISM.

By *allotropy* is understood the phenomenon presented by several elements which are capable of existing in two or more distinct forms, each of which exhibits well-marked characteristics of its own, different from those of the other modifications. For example, we have the matter of sulphur producing the distinct substances called respectively, octahedral, prismatic, and plastic sulphur. Oxygen also occurs as common oxygen gas and ozone ; carbon as charcoal, graphite, and diamond ; phosphorus as crystallised white and red varieties of the element.

In each of these cases the several modifications differ from one another, not in the material of which they consist, but in colour, crystalline form, density, and other physical characters ; also in the amount of energy associated with the matter. The evidence of this is to be found in the modes of formation of the less stable from the more stable varieties, and in the different amounts of heat produced in the combination of these several varieties with oxygen or chlorine, or some other element. In the combustion of carbon, for example, in oxygen, the amount of heat evolved differs with each allotropic form. The amount of heat is estimated by observation of the amount of water, the temperature of which is raised through a given range of some thermometric scale.

Grams of Water heated 1° *C. by burning* 1 *Gram of*

Diamond, ...	7770
Natural Graphite, . . .	7797
Wood Charcoal, . . .	8080

With these physical differences are usually associated some notable differences in chemical behaviour. In the case of carbon, for example, the diamond, even in the form of powder, is unaffected by sulphuric acid or nitric and chloric acids; graphite is converted by the same mixture into a yellow crystalline substance, graphic acid; while charcoal yields a black liquid which, by the continued action of the oxidising agent, gives up the whole of the carbon in the form of its gaseous oxides.

The cases thus far referred to are those of elements, but something analogous occurs in certain chemical compounds. The dimorphism of calcium carbonate and of mercuric iodide, already referred to, as well as the similar phenomena exhibited by other substances, may perhaps be included in the same category, but the most remarkable facts are to be observed in connection with compounds of carbon. It was discovered early in the present century, so soon as methods became known for determining accurately the composition of carbon compounds, that the same elements combined together in the same proportion may yet give rise to compounds having wholly different properties. Compounds having this relation to one another are said to be *isomeric*.* One of the first examples of this kind was discovered in 1828, when it was found that ammonium cyanate, NH_4CNO was converted by a gentle heat, but without gain or loss of any constituent, into urea or carbamide, $CO(NH_2)_2$. Another good example is afforded by the hydrocarbons called terpenes, all of which have the composition represented by the formula $C_{10}H_{16}$; but one of them constitutes spirit of turpentine (boiling-point, 156°), while another is the chief constituent of essence of lemon (boiling-point, 176°), a liquid of wholly different odour, density, and chemical habit.

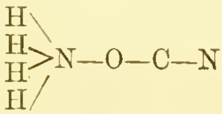
In some cases the same composition is preserved, but the molecular weight is greater in one compound than in another. For example, nitric peroxide at low temperatures has the molecular formula N_2O_4, while at high temperatures it is NO_2; cyanogen gas is C_2N_2, while paracyanogen is C_nH_n, where n is greater than 2. Turpentine oil, $C_{10}H_{16}$, when heated moderately, is converted into a viscid liquid of very high boiling point, the molecular constitution of which may be expressed as $(C_{10}H_{16})n$, while if heated to low redness the $C_{10}H_{16}$ splits into two parts and yields a very volatile liquid called isoprene, which has the formula C_5H_8. In all such cases the different isomeric compounds are said to be *polymeric*,† in reference to the fact that the molecular weight of the one compound is a multiple of the molecular weight of the other.

It is generally observed that when the same elements are united to form aggregates of different degrees of complexity, the more complex molecules form substances of greater density, higher boiling point or less volatility, and less solubility than the more simple. The knowledge of this fact seems to point to an explanation of the differences noticed in the allotropic modifications of the elements. Thus red

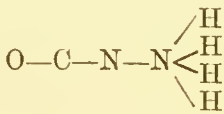
* Ἴσος, equal μέρος.
† πολύς, many; μέρος, part.

phosphorus is insoluble in carbon bisulphide and other liquids which dissolve white phosphorus; it is also less fusible and has a higher density than the more active white allotrope. This is probably a case of polymerism, the red phosphorus having a relation to white phosphorus analogous to that which subsists between paracyanogen and cyanogen.

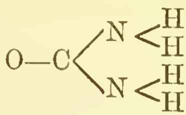
Among carbon compounds, the constitution of which has been generally more carefully studied than that of any other class, the isomerism may often be accounted for in a different way. It is attributed to a different arrangement of the atoms in the molecule, the molecular weight remaining unaltered. Thus in the case of ammonium cyanate and urea there is no reason to suppose a difference in the molecular weights of these two compounds, the composition of each being fully expressed by the symbols CH_4N_2O. But while in the cyanate the atoms are distributed in one of the following ways:



or



In urea the atoms are linked together thus:



Such compounds are said to be *metameric*.

It is probable that some examples of this diversity of arrangement are to be found among 'inorganic' compounds, but their investigation is far more difficult. One case of the kind is probably afforded by the violet and green chromic sulphates. If violet crystalline chrome alum, $K_2SO_4,Cr_2(SO_4)_3 24H_2O$, is dissolved in water and the solution boiled for some time, not only does the colour of the solution become bright green and the liquid refuse to crystallise, but on the addition of barium chloride in excess, the whole of the sulphate is not precipitated, as would be the case if the salt retained its original and normal constitution. The green solution kept at common temperatures slowly reassumes its violet colour and capacity for crystallisation.

HEAT AND CHEMICAL AFFINITY.

Whatever may be the nature of chemical affinity, one important fact is clearly established with regard to it; namely, that its manifestations are always accompanied by the evolution or absorption of heat. Change of composition, or chemical action, and heat are mutually convertible; a given amount of chemical action will give rise to a certain definite amount of heat, which quantity of heat must be directly or indirectly expended, in order to reverse or undo the chemical action that has produced it. The production of heat by chemical action, and the definite quantitative relation between the amount of heat evolved and the quantity of chemical action which takes place, are roughly indicated by the facts of our most familiar experience; thus, for instance, the only practically important method of producing heat artificially consists in changing the elements of wood and coal, together with atmospheric oxygen, into carbon dioxide and water; and every one knows that the heat thus obtainable from a given quantity of coal is limited, and is, at least approximately, always the same. The accurate measurement of the quantity of heat produced by a given amount of chemical action is a problem of very great difficulty; chiefly because chemical changes very seldom take place alone, but are almost always accompanied by physical changes, involving further calorimetric effects, each of which requires to be accurately measured and allowed for, before the effect due to the chemical action can be rightly estimated. Thus the ultimate result has, in most cases, to be deduced from a great number of independent measurements, each liable to a certain amount of error. It is therefore not surprising that the results of various experiments should differ to some extent, and that uncertainty should still exist as to the exact quantity of heat corresponding with even the simplest cases of chemical action.

The experiments are made by inclosing the acting substances in a calorimeter, surrounded by water or mercury, the rise of temperature in which indicates the quantity of heat evolved by the chemical action, after the necessary corrections have been made for the heat absorbed by the containing vessel and the other parts of the apparatus, and for the amount lost by radiation, etc. For the construction of these instruments and the methods of observation the reader must refer to works on Heat.

The following table gives the quantities of heat, expressed in heat-units, evolved in the combustion of various elements, and of a few compounds, in oxygen, referred: (1) to 1 gram of each substance burned; (2) to 1 gram of oxygen consumed; (3) to 1 atom or molecule (expressed in grams), of the various substances.

The unit of heat here adopted is the quantity of heat required to raise 1 gram of water from 0° to 1° C.

Heat of Combustion of Elementary Substances in Oxygen.

Substance.	Product.	Units of Heat or Calories Evolved. By 1 Gram of Substance.	By 1 Gram of Oxygen.	By 1 Atom of Substance.	Observer.
Hydrogen,	H_2O	33881	4235	33881	Andrews.
		34462	4308	34462	Favre & Silbermann.
Carbon—					
Wood-charcoal,	CO_2	7900	2962	94800	Andrews.
		8080	3030	96960	Favre & Silbermann.
Gas-retort carbon,	,,	8047	3018	96564	,,
Native graphite,	,,	7797	2924	93564	,,
Artificial graphite,	,,	7762	2911	93144	,,
Diamond,	,,	7770	2914	93940	,,
Sulphur—					
Native,	SO_2	2220	2220	71040	,,
Recently melted,	,,	2260	2260	72320	,,
Flowers,	,,	2307	2307	73821	Andrews.
Phosphorus—					
(Yellow)	P_2O_5	5747	4454	178157	,,
Zinc,	ZnO	1330	5390	86450	,,
Iron,	Fe_3O_4	1582	4153	88592	,,
Tin,	SnO_2	1147	4230	135360	,,
Copper,	CuO	603	2394	38304	,,

The following results have been obtained by the complete combustion of partially oxidised substances :—

Substance.	Product.	Units of Heat Evolved. By 1 Gram of Substance.	In the Formation of 1 Molecule of the Ultimate Product.	Observer.
Carbon monoxide, CO	CO_2	2403	67284	Favre & Silbermann.
		2431	68064	Andrews.
Stannous oxide, SnO	SnO_2	519	69584	,,
Cuprous oxide, Cu_2O	CuO	256	18304	,,

The three substances in this table contain exactly half as much oxygen as the completely oxidised products; and on comparing the amount of heat evolved in the formation of one molecule of stannic or cupric oxide from the corresponding lower oxide, with the quantity produced when a molecule of the same product is formed by the complete oxidation of the metal in one operation, we find that the combination of the second half of the oxygen contained in these bodies evolves sensibly half as much as the combination of the whole quantity. In the formation of carbon dioxide, however, the second half of the oxygen appears to develop more than two-thirds of the total amount of heat; but this result is probably due, in part at least, to the fact that when carbon is burned into carbon dioxide, a considerable but unknown quantity of heat is expended in converting the solid carbon into gas, and thus escapes measurement; while, in carbon monoxide, the carbon already exists in the gaseous form, and therefore no portion of the heat evolved in the combustion of this substance is similarly expended in producing a change of state.

It seems probable, also, that a similar explanation may be given of the inequalities in the amounts of heat produced by the combustion of different varieties of pure carbon and sulphur—that is to say, that a portion of the heat generated by the combustion of diamond and graphite goes to assimilate their molecular condition to that of wood-charcoal, and that there is an analogous expenditure of heat in the combustion of native sulphur.

The quantities of heat evolved in the combination of chlorine, bromine, iodine, and other elements, with one another, and in many other chemical changes, such as the neutralisation of acids by bases, the solution of salts in water and in other liquids, have been determined by Favre and Silbermann, Andrews, and others, and especially by Berthelot and by Thomsen; but we must refer to larger works for the full results.

The thermal effects which may result from the reaction of different substances on one another in presence of water, are more complicated than those resulting from direct combination. In addition to the different specific heats of the reagents and products, and to the different quantities of heat absorbed by them in dissolving, or given out by them in combining with water, the conversion of soluble substances into insoluble ones, as a consequence of the chemical action, or the inverse change of insoluble into soluble bodies, are among the secondary causes to which part of the calorimetric effect may be due in these cases.

When a gas dissolves in water, the heat due to the chemical action is augmented by that due to the liquefaction of the gas; so also when a solid body is dissolved in water, the total thermal effect is due in part to the chemical action taking place between the water, and the solid, and in part to the liquefaction of the substance dissolved. In the former case the chemical and physical parts of the phenomena both cause evolution of heat; in the latter case the

physical change occasions disappearance of heat, and if this effect is greater than that due to the chemical action, the ultimate effect is the production of cold, and this is often observed.

In order to separate two masses which attract each other, work has to be done, which is recoverable in the form of mechanical force, or in the form of heat, when the bodies come together again. The energy which is put into a mass of ice when it is converted into water, is only latent, and is reproducible as sensible heat when the water freezes. So also the evaporation of a liquid can only be effected at the expense of kinetic energy, which becomes potential in the resulting vapour. All that is known of chemical combinations and separations tends to show that these changes are subject to the same rule : namely, that *combination between two atoms or molecules is always attended by evolution of heat, and that the separation of bodies thus united can only be accomplished by supplying from without an amount of heat equal to that which is disengaged in their union.* If this is true, the energy of chemical separation, or "chemical affinity," should be measurable by the amount of heat evolved in chemical combinations. Unfortunately, as already indicated, this appears at present to be impossible. If we consider the action which occurs between any two of the so-called elements, and even in those cases in which we recognise a change of state from solid to liquid, liquid to gas, and so forth, and can allow for this change, we never find that the case can be truly represented as one of simple combination of atoms. Take hydrogen and oxygen for example. The change which occurs in their combustion is not

$$2H + O = H_2O + 34C \text{ *}$$

but

$$\begin{array}{cccccccc} H & & O & & H & & H.O.H & \\ . & + & . & + & . & = & & + 34C. \\ H & & O & & H & & H.O.H & \end{array}$$

Whence it is obvious that the heat evolved represents only the balance of surplus energy remaining over after H has been separated from H in two molecules of hydrogen, and O separated from O in a molecule of oxygen. Both these operations involve the consumption of an unknown amount of energy, which, however, is less than that given out by combination of 2H with O twice over by the amount 34C.

The result in this case is said to be *exothermic*, for heat is actually evolved, producing rise of temperature. From the principle already enunciated, the greater the amount of heat evolved in the reaction, the more stable will be the resulting products. It was formerly supposed that combination could occur only between dissimilar atoms, but we now know that not only may atoms of the same kind unite together to form very stable molecules, but that, in certain cases, such combinations are more difficult to break up than those of dissimilar

* For the sake of simplicity the figures given in the tables are here divided by 1000. C=calorics.

elements. A consequence of this is, that combinations between certain pairs of elements can only be brought about by indirect processes, and the compounds thus formed contain more energy than the elementary molecules from which they were produced. Hence in such combinations heat is not evolved, but a certain amount is absorbed, and the change is said to be *endothermic.* In cases of this kind, the amount of heat which is absorbed in the process of combination cannot usually be directly determined, but what is called the heat of formation may be ascertained in one way by observing the amount of heat given out when the compound is resolved into its constituents. Thus the combination

$$H_2 + I_2\,(\text{solid}) = 2HI\,(\text{gas}),$$

is said to be attended by absorption of 12 calories.

The facts observed are, however, better expressed by the equation

$$2HI\,(\text{gas}) = H_2 + I_2\,(\text{solid})\;(+\;12C)$$

which shows that the decomposition of hydrogen iodide is accompanied by the evolution of heat.

Another mode of proceeding to estimate the heat of combination, in such a case as that of hydrogen and iodine, is as follows :—First the heat of solution of the compound HI in water is determined, and found to be

$$HI + 400H_2O = +19C.$$

Then the action of iodine upon hydrogen sulphide is studied, and it is observed that iodine, solid or dissolved in carbon bisulphide, will not act upon hydrogen sulphide in the gaseous state at any temperature below that at which the H_2S is decomposed, but iodine does act upon hydrogen sulphide in the presence of much water, and with evolution of heat.

$$\underbrace{2H_2S + 2I_2}_{\text{in water.}} = \underset{\text{dissolved.}}{4HI} + \underset{\text{solid.}}{S_2}\,(+\;34C).$$

A part of the heat evolved,* viz., $19 \times 4 = 76$, is due to the solution of the 4HI in water. The separation of the S from H_2 in presence of water is known to be attended by absorption of $9 \times 2 = 18C$. Introducing these values into the equation, we find that of the heat produced in the reaction (76), a part is employed in the separation of the S from the H_2 (18), a part becomes sensible to the thermometer, raising the temperature of the liquid (34), while the balance goes to the 4H and 4I which combine

$$76 - (18 + 34) = 24.$$

* In this rough estimate, the heat evolved in consequence of the precipitation of solid sulphur, and the heat absorbed in the solution of the solid iodine, are neglected.

So that the heat absorbed in combination of H with I must be approximately $\frac{24}{4}$ or 6C, which agrees with the result of the other method.

It is instructive to compare this result with the corresponding combinations of chlorine and bromine, which can be effected directly :

$$H + Cl + 400H_2O = HCl400H_2O + 39C.$$
$$H + Br + 400H_2O = HBr400H_2O + 28C.$$
$$H + I + 400H_2O = HI400H_2O + 13C.$$

If in each case the observed heat of dissolution of the hydracid in water is deducted, the following are the values obtained :

	Heat of solution.		Heat of formation of the gas.
HCl	39 – 17	=	+22C
HBr	28 – 20	=	+ 8C
HI	13 – 19	=	– 6C.

These results accord with everyday experience of the general behaviour of these compounds, and together with many others of similar kind lead to the recognition of a general principle which may be stated broadly as follows :—In any mixture of materials placed under such conditions of temperature, &c., that the bodies present may act upon one another, if two or more rearrangements are possible, *those compounds will be formed in the production of which the greatest evolution of heat occurs*, and will continue to be formed until the conditions are so altered as to put a stop to the action. We know, for example, that chlorine displaces bromine from all its compounds with metals and with hydrogen, and that both chlorine and bromine act similarly towards iodine. We know that hydrogen will burn in chlorine gas, but that in bromine vapour it will not burn unless the temperature of both be raised, while hydrogen will not only not burn under any known circumstances in iodine vapour, but that when these are mixed together and gently heated combination ensues very slowly. Hydrogen iodide is completely decomposed below a red heat, and in the presence of air it gives up iodine at common temperatures. In solution it acts as a powerful reducing agent, iodine being set free, though the extent of dilution materially affects its action in this respect, a strong or saturated solution being most easily decomposed, while the acid is more stable when much water is present. And it is found that the reaction between iodine and hydrogen sulphide proceeds freely in the presence of water only so long as the proportion of water is relatively large. As the hydriodic acid accumulates in the liquid and the proportion of water therefore relatively less, the action slackens, and finally ceases altogether when the solution contains about 50 per cent. of hydrogen iodide, and has a density 1·56. If a solution of hydriodic acid stronger than this be made otherwise, the addition of solid sulphur to the liquid causes an immediate liberation of iodine and evolution of hydrogen sulphide.

The dissolution of salts and other solids in liquids is an act which is always accompanied by thermal change, made manifest by the evolution or absorption of heat. Thus if sulphuric or phosphoric oxide is dissolved in water, or anhydrous chloride of iron, calcium, or zinc, dry sodium carbonate or sodium sulphate is dissolved in the same liquid, heat is given out. In cases such as these there can be no reasonable doubt that the heat evolved is mainly the result of chemical combination taking place between the solid and the solvent. The following examples exhibit the amount of heat, which is sometimes considerable, thus produced in the dissolution of the several salts in a relatively large volume of water at the temperature 18°.

Formula of Salt.	Ratio of Water to Salt in Molecules.	Heat of Dissolution at 18° Calories.
K_2CO_3	400	6490
Na_2CO_3	400	5640
Na_2HPO_4	400	5640
$BaCl_2$	400	2070
$CaCl_2$	300	17410
$MgCl_2$	800	35920
$MgSO_4$	400	20280
$ZnCl_2$	300	15630
$FeCl_2$	350	17900
$FeCl_3$	1000	31680
$CuCl_2$	600	11080

These examples are sufficient to show that a very energetic action often occurs, and that, to judge by the heat evolved in the act, a very stable compound may result. This is the case, though it may be observed that the evolution of much heat in the process of solution does not indicate that the salt will combine with a large *quantity* of water. This may be noticed in the two salts first mentioned, namely, the carbonates of potassium and sodium. The former retains, when in the solid state, only about 1 molecule of water; the latter, though it crystallises with $10H_2O$, gives in the process of dissolution somewhat less heat than the potassium salt.

On the other hand, there is a very large number of cases in which the act of dissolving a solid salt in water is attended by absorption of heat. The following are some examples. (*See* Table, p. 289.)

Here, too, a reason can be at once assigned for the greater part of the thermal effect, namely, the change of condition from solid to liquid when the salt dissolves. The mere latent heat of fusion is, however, not sufficient in the few cases which have been examined to account for the whole. Potassium nitrate, for example, melts at 339°, and in the act of melting, each molecular weight absorbs 4787·4 calories, which is only a little more than half the amount of heat

Formula of Salt.	Ratio of Water to Salt in Molecules.	Heat of Dissolution at 18° Calories.
KNO_3	200	– 8520
$KClO_3$	400	– 10040
K_2SO_4	400	– 6380
NaCl	100	– 1180
$Na_2CO_3 10H_2O$	400	– 16160
$Na_2HPO_4 2H_2O$	400	– 390
$Na_2HPO_4 12H_2O$	400	– 22830
$CaCl_2 6H_2O$	400	– 4340
$MgSO_4 7H_2O$	400	– 3800

absorbed in dissolving the same amount of the salt in water. The difference may be accounted for by noticing that energy is consumed, not only in the change of solid salt into liquid (fusion), but in the intermixture of the separated salt molecules with those of the water, also in the process which attends the introduction of the salt, consisting in the breaking up of the groups of water molecules into simpler groups, a process which is analogous to volatilisation. When a solid is thus made to liquefy by a relatively weak chemical attraction, cold usually results. This is the principle of freezing mixtures.

When snow or powdered ice is mixed with common salt, and a thermometer plunged into the mass, the mercury sinks to 0° F. (–17·7° C.), while the whole after a short time becomes fluid ; such a mixture is very often used in chemical experiments to cool receivers and condense the vapours of volatile liquids. Powdered crystallised calcium chloride and snow produce cold enough to freeze mercury. Even powdered potassium nitrate, or sal-ammoniac, or ammonium nitrate, dissolved in water, occasions a very notable depression of temperature ; in every case, in short, in which solution is unaccompanied by energetic chemical action, cold is produced, and even some cases in which notable chemical reactions occur, also lead to reduction of temperature when the sum of the endothermic effects exceeds the sum of the exothermic effects attending the change. Thus a mixture of crystallised sodium sulphate and strong aqueous hydrochloric acid forms a mixture capable of giving a reduction of temperature amounting to some 30° below the ordinary temperature—the reduction of temperature in this case being mainly due to the liquefaction of the water of crystallisation of the salt, the effect of which more than compensates for the heat-evolution attending the conversion of the sulphate into chloride of sodium.

As a general rule, a salt which, on being dissolved in water, gives out heat, gives a further amount when its solution is diluted ; and, on the other hand, salts which in dissolving absorb heat usually absorb a further amount when the solution is diluted. The thermal change, positive or negative, becomes less and less as the liquid is

diluted, though it is often recognisable even after the addition of several hundreds of molecules of water to one molecule of salt.

The heat produced during the neutralisation of acids by alkalis has been the subject of much research, and has led to some interesting results. The following table includes the values assigned by Julius Thomsen to the heat change attending the neutralisation of the more common acids :—

Heat of Neutralisation of Acids by Soda in presence of Water,

$$H\bar{R} + NaHO = Na\bar{R} + H_2O.$$

	Calories.
HCl,	13740
HBr,	13748
HI,	13721
HF,	16272
HNO_3,	13617
H_3PO_2,	15160
HPO_3,	14510
$\frac{1}{2}H_2SO_4$,	15690
$\frac{1}{2}H_3PO_3$,	14228
$\frac{1}{3}H_3PO_4$,	11343
$HCHO_2$ (formic acid),	13450
$HC_2H_3O_2$ (acetic acid),	13400
$\frac{1}{2}H_2C_2O_4$ (oxalic acid),	13840

When a polybasic acid is neutralised by an alkali introduced in successive doses, the exchange of the metal for the several atoms of hydrogen of the acid is not usually attended by the evolution of the same amount of heat. Thus when sulphuric acid is neutralised by soda the amount of heat evolved per molecule of NaHO added, is as follows :

$$\left.\begin{array}{l} NaHO.Aq + H_2SO_4Aq = +14754 \\ 2NaHO.Aq + H_2SO_4Aq = +31378 \end{array}\right\} \text{Difference, 16624.}$$

The second molecule of NaHO seems to give more heat than the first.

In the case of orthophosphoric acid, however, the addition of

The first molecule of NaHO to H_3PO_4 gives	+ 14289
The second molecule of NaHO to the preceding mixture	+ 12249
The third molecule of NaHO to the preceding mixture	+ 6951

This seems to agree with the fact that the solutions of the di- and tri-sodium phosphates in water are strongly alkaline, and probably contain free sodium hydrate formed by the action of the water on the salt.

The heat of neutralisation of acids by alkalis has, however, received another interpretation which will be referred to again when the phenomena of electrolysis have been discussed.

ELECTROLYSIS.

Electro-chemical Theories.

Electrolysis.—When an electric current produced by any means whatever is made to pass through a solid, one of the following effects ensues ; (1) The current is conducted with practically no loss by such substances as silver or copper when rods of sufficient thickness are used ; (2) resistance is offered by the substance, and the energy of the current is more or less completely converted into heat, as is the case with the metals platinum, bismuth, and the solid non-metals carbon, &c.

If the solid is replaced by a liquid, the current may be (1) entirely stopped by such liquids, as dry petroleum, anhydrous hydrogen, chloride, &c., (2) it may pass without loss and without chemical effect through mercury and other molten metals, or (3) it may cause decomposition of one or more constituents of the liquid. This last process which is called *electrolysis** occurs when a current is made to traverse solutions of acids or metallic salts, also many metallic compounds when melted. Examples of electrolysis such as the decomposition of acidulated water, of solution of common salt, and of strong hydrochloric acid, have already been supplied earlier in the book.

In order that electrolysis may occur, the substance must be in the liquid state. Lead chloride for example, if melted in a crucible, conducts a current freely, and gives up its elements, lead and chlorine at the electrodes or wires by which the current passes into the fused mass ; but if the source of heat is withdrawn and the salt allowed to solidify in the crucible, decomposition at once ceases, and if a galvanometer is included in the circuit, it becomes evident that the current is no longer passing. Similarly, ice arrests the passage of a current.

A compound is, however, not necessarily an electrolyte because it is liquid. Thus, pure dry liquid hydrogen chloride and liquid stannic chloride are incapable of conducting, and only undergo electrolytic decomposition when the current passes through them after addition of water.

During electrolysis, the elements are disengaged solely at the limiting surfaces of the liquid, where, according to the common mode of speech, the current enters and leaves the latter, all the intermediate portions appearing perfectly quiescent. If, while the decomposition is rapidly proceeding, the intervening liquid be examined by a beam of light, or by other means, not the slightest disturbance or movement of any kind will be perceived ; nothing like currents in the liquid or bodily transfer of gas from one part to another can be detected.

* From ἤλεκτρον, and λύειν, to loose.

In addition, the elements are not separated indifferently and at random at these two surfaces, but make their appearance with perfect uniformity and constancy at one or the other, according to their chemical character, namely, oxygen, chlorine, iodine, acids, &c., at the surface connected with the platinum, carbon, copper, or *positive* end of the battery ; hydrogen, and the metals, at the surface in connection with the zinc, or *negative* extremity of the arrangement.

The former is called the *anode*, and the substances disengaged from this surface are often spoken of as anions or as *electro-negative ions*, while the wire at which hydrogen and metals make their appearance is called the *cathode*, and the *ions* or elements which collect there are called cathions or as *electro-positive* elements.

Not only is electrolysis definite in direction, it is also definite in amount, and of the quantitative laws established by the researches of Faraday, the two following are of great importance to the student of chemistry.

1. *The amount of chemical decomposition is proportional to the strength of the current*, or the quantity of any ion set free in a given time is proportional to the strength of the current.

2. *Ions are liberated by the same current in quantities which are proportional to their chemical equivalents.*

The same current which decomposes 9 parts by weight of water will separate the elements in 166 parts of potassium iodide, and will cause the deposition of the metal from 79·5 of cupric sulphate. Hence to calculate the amount of any simple or compound ion liberated by a current, it is only necessary to divide its atomic weight by the number which expresses its valency. For example, if 1 part by weight of hydrogen is liberated in one cell of any circuit which includes a battery, and a series of separate vessels containing different solutions, the quantities of the elements liberated will be as follows :—

	Atomic Weight.	Valency.	Equivalent.
Oxygen,	16	2	8
Chlorine,	35·5	1	35·5
Iodine,	127	1	127
Sodium,	23	1	23
Copper,	63	2	31·5
Mercury,	200	2	100
&c.	&c.	&c.	

In the case of oxy-salts which contain compound salt radicles, such as sulphates and nitrates, the initial stage in the process of decomposition by the current appears to be the same as that of the haloid salts ; copper chloride, for example, is divided into its two elements,

$$Cu \text{ and } 2Cl,$$

and cupric sulphate into the ions

$$Cu \text{ and } SO_4.$$

In such cases the substances actually obtained are the metal at the

cathode, and oxygen at the anode, for the SO_4 in the presence of water is immediately resolved into sulphuric acid and water; $SO_4 = SO_3 + O$ and $SO_3 + H_2O = H_2SO_4$.

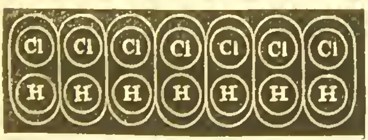
In many cases secondary products occur as the result of the action of the liberated ion upon the water or other medium in the midst of which it is set free. Thus when an aqueous solution of common salt is electrolysed, the products are not metallic sodium and chlorine, but sodium hydroxide and hydrogen at the cathode, while chlorine is set free at the anode if the solution is strong, or hydrogen chloride is formed and oxygen given off if the solution is dilute. Hence the earlier experimenters were led to the conclusion that salts such as potassium and sodium sulphate were made up of the alkali-metal oxide or *base* and a non-metallic oxide, then regarded as the *acid*. Thus,

$$\underset{\text{Sodium Sulphate.}}{Na_2O\,SO_3} = \underset{\text{Soda.}}{Na_2O} + \underset{\text{Sulphuric Acid.}}{SO_3}.$$

To all other metallic salts a similar constitution was attributed, the precipitation of the metal, and not of the metallic oxide, being supposed due to the simultaneous action of hydrogen formed by the decomposition of water.

In order to account for the appearance of the products of electrolysis upon the surface of the electrodes only, and not at any intervening portion of the liquid, the following hypothesis put forward in 1805 by Grotthuss, has been, until of late years, very generally adopted. The hypothesis supposes that in a solution of, for example, hydrogen chloride, the molecules of this compound are moving about in all conceivable directions, but that immediately two metallic wires or plates at different electrical potential are introduced, the molecules between them become ranged in chains which extend across the liquid from one plate to the other. The atoms forming these molecules then undergo a process of transfer from molecule to molecule, as shown in the two following diagrams, in which it is seen that the hydrogen travels

Fig. 106.



Hydrochloric acid immediately before electrolysis.

Fig. 107.

Hydrochloric acid undergoing electrolysis.

in the one direction while the chlorine travels in the opposite direction, and neither becomes free till it reaches the end of the chain of molecules and arrives at the surface of the electrode, from which it is disengaged in the form of gas.

An important modification has of late years been introduced into this hypothesis. It is now assumed by many physicists that a solution of, for example, hydrogen chloride in water contains, not entire molecules of that compound, or comparatively few of them, but the ions or products of its dissociation distributed throughout the liquid.

These free atoms are supposed to carry charges of positive and negative electricity, and unite when they approach one of the opposite kind. Molecules of the compound hydrogen chloride are thus formed temporarily, but the ions immediately afterwards dissociate again. When the electrodes are introduced the hydrogen ions with their positive charge are drawn to the negative pole, while the chlorine ions being charged negatively, go to the positive. According to this view the action of the 'current' is merely to cause the movement of the already separated ions to the surfaces of the electrodes, where they give up their electricity and join up in couples, or otherwise, to form ordinary molecules of the elementary substances hydrogen and chlorine, in the form in which they are alone known to us.

It was supposed by Berzelius and by Davy that chemical combination is due to the attraction of oppositely electrified atoms; that hydrogen, for example, having au inseparable charge of positive electricity, was capable of combining only with substances such as chlorine or oxygen, the atoms of which have a similar negative charge, electric neutrality resulting from the close approximation of the two. This view, however, is surrounded by difficulties. It seems also to be incompatible with the dissociation hypothesis just mentioned, for supposing two hydrogen atoms to arrive at the negative electrode, or in any other way to be brought near to each other, there seems to be no reason why being *similarly* charged they should unite, or if they did combine, why the resulting couple should not show signs of electrical, that is of chemical, activity, twice as great as the single atoms. We know, however, that this is not the case, hydrogen gas being singularly inert, and the belief that the atoms of hydrogen do unite to form hydrogen molecules is both well founded and very generally accepted.

The supporters of the dissociation hypothesis attribute the chemical activity of many substances, especially acids and bases, to the state of dissociation in which they are supposed to subsist in their solutions. A 'strong' acid, for example, is one in which the complete molecules are few and the ions more generally dissociated than is the case in a 'weak' acid. This hypothesis is, therefore, necessarily associated with another, as to the nature of the change which occurs when an acid is neutralised by an alkali. The action of soda on hydrochloric acid, for example, is not

$$NaHO + HCl = NaCl + HHO;$$

but soda, acid, and resulting salt being alike dissociated, while the water, a very neutral and inactive substance, is supposed to be dissociated not at all, or to a very small extent, the only chemical combination which occurs in the process is between the hydrogen of the acid and the hydroxyl HO of the alkali.

$$Na + HO + H + Cl = Na + Cl + HHO.$$

Hence it follows that the heat which is evolved in this operation must be due solely to the formation of water. On referring to the

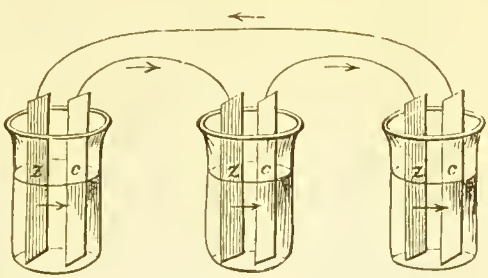
table (p. 290) in which is given the heat of neutralisation of various acids by soda in the presence of water, it will be seen that the evolution of heat is nearly uniform, the majority of acids giving between 13,000 and 14,000 calories per molecule of soda.

Theory of the Voltaic Battery.—The metals of voltaic batteries are usually zinc for the active metal, and copper, silver, or platinum, for the inactive one : the greater the difference of chemical activity the greater the difference of electrical potential, and, consequently, the greater electromotive force and the more active the battery as a source of electricity. Hard carbon is often substituted for the inactive metal. The liquid is usually dilute sulphuric acid.

The figure (108) represents the first and simplest form of battery or "crown of cups" invented by Volta. A number of cups or glasses are arranged in a row or circle, each containing a piece of active and a piece of inactive metal, and a portion of exciting liquid—zinc, copper, and dilute sulphuric acid, for example. The copper of the first cup is connected with the zinc of the second, the copper of the second with the zinc of the third, and so to the end of the series. On establishing a communication between the first and last plates by means of a wire, or otherwise, a current is established.

In every form of such apparatus, however complex it may appear, the direction of the current may be easily understood and remembered. When both ends of the series are insulated, the zinc end exhibits negative, the copper or platinum end positive electricity : consequently, when the two extremities are joined by a conducting wire, the current of positive electricity proceeds *without* the battery from the platinum or copper to the zinc, and *within* the battery, from the zinc to the copper or platinum, as indicated by the arrows.

Fig. 108.



While the circuit remains broken, the zinc is perfectly inactive, no acid is decomposed, no hydrogen liberated ; but the moment the connection is completed, bubbles of hydrogen arise, not from the zinc, but from the copper or platinum surfaces alone, while the zinc dissolves quietly. The acid undergoes electrolysis, its hydrogen appearing at the negative plate, and its sulphion, SO_4, uniting with the substance of the positive zinc.

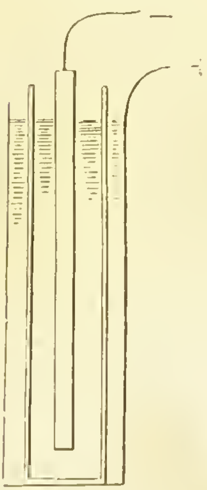
Common zinc is very readily attacked and dissolved by dilute sulphuric acid. This arises from the formation of a multitude of little voltaic circles, by the aid of particles of foreign metals partially imbedded in the zinc. This gives rise in the battery to what is called local action, by which, in the common forms of apparatus, three-

fourths or more of the metal is often consumed, without contributing in the least to the general effect, but, on the contrary, injuring it to some extent. This evil is got rid of by amalgamating the surface so as to cover up the particles of foreign metal and constantly present a fresh surface of zinc.

By experiments, in which local action was avoided, it has been proved that the quantity of electricity set in motion by the battery varies with the zinc dissolved. Coupling this fact with that of the definite action of the current, it will be seen that when a perfect battery of this kind is employed to decompose hydrochloric acid, in order to evolve 1 gram of hydrogen from the latter, 32·5 grams of zinc must be dissolved as chloride, and its equivalent quantity of hydrogen disengaged in each active cell of the battery,—that is to say, that the electricity generated by the solution of an equivalent of zinc *in* the battery is capable of effecting the decomposition of an equivalent of hydrochloric acid or any other electrolyte *out* of it.

In all the older forms of the voltaic battery, such as Volta's, Cruickshanks', and Wollaston's, in which two metals, zinc and copper, are immersed in a single exciting fluid, the power rapidly decreases. This loss of power depends, partly on the gradual change of the sulphuric acid into zinc sulphate, but still more on the coating of hydrogen, and, at a latter stage, on the precipitation of metallic zinc on the copper plates. It is evident that if the copper plate in the liquid became covered with zinc, it would act electrically like a zinc plate.

Fig. 109.



To prevent this alteration of the negative plate, and consequent loss of electric power, it is necessary either to remove the hydrogen as fast as it accumulates, or to prevent its evolution altogether, and for this purpose various forms of battery have been devised.

Daniell's Battery.—In this form of battery (fig. 109) each cell consists of a copper cylinder within which is placed a hollow cylinder of unglazed earthenware, in the axis of which is placed a rod of amalgamated zinc. This inner cylinder is filled with a mixture of 1 part by measure of oil of vitriol and 8 of water, and the exterior space with the same liquid saturated with copper sulphate. A sort of little colander is fitted to the top of the cell, in which crystals of the copper sulphate are placed, so that the strength of the solution may remain unimpaired. When a communication is made by a wire between the rod and the copper cylinder, a strong current is produced, the power of which may be increased to any extent by connecting a sufficient number of such cells into a series, on the principle of the crown of cups, the copper of the first being attached to the zinc of the second.

By this arrangement the accumulation of hydrogen and deposition of zinc on the surface of the copper plate is altogether avoided ; the zinc in the porous cell, whilst it dissolves in the sulphuric acid, decomposes it, but does not liberate any hydrogen ; for at the boundary of the copper solution, the hydrogen takes the place of the copper, and thus copper is precipitated on the copper plate which simply increases in thickness while constantly preserving the same kind of surface.

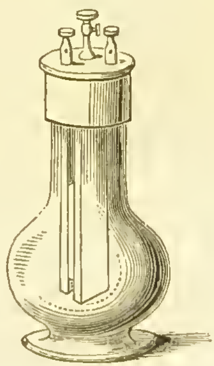
Grove's Battery.—This form of battery has nearly double the electromotive force of Daniell's. One of the cells is represented in fig. 110. The zinc plate is bent round, so as to present a double surface, and is well amalgamated : within it stands a thin flat cell of porous earthenware, filled with strong nitric acid, and the whole is immersed in a mixture of 1 part by measure of oil of vitriol and 8 of water, contained in a separate cell of glazed porcelain. The arrangement is completed by a strip of platinum foil, which dips into the nitric acid. In this cell there is no "polarisation" : for the hydrogen, in passing through the nitric acid in its progress towards the platinum plate, decomposes the nitric acid, and is itself oxidised to water, while nitrogen peroxide is formed and remains dissolved in the nitric acid.

Fig. 110.

Bunsen has modified the Grove battery by substituting for the platinum dense charcoal or coke, which is an excellent conductor of electricity. By this alteration, at smaller expense, a battery is made which is much in use and nearly as powerful as that of Grove.

Zinc-carbon batteries with a single liquid are often employed.—In the *Dichromate battery*, an ordinary form of which is represented in fig. 111, a zinc plate placed between two gas-carbon plates is immersed in a mixture of dilute sulphuric acid and potassium dichromate, this salt acting as a depolariser by oxidising the hydrogen evolved at the surface of the zinc plate. This solution, however, acts upon the zinc, even when the poles are disconnected, and to prevent this, the zinc plate is fixed to a rod by which it can be drawn up out of the liquid when the battery is not in use.

Fig. 111.

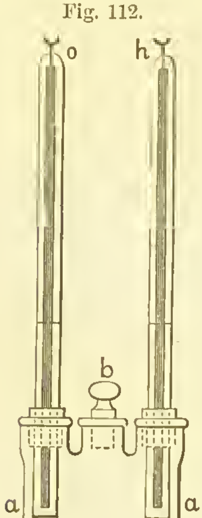


In *Leclanché's battery*, the exciting liquid is a solution of sal-ammoniac, NH_4Cl. The zinc dissolves in it, with formation of zinc-ammonium chloride, $Zn(NH_3Cl)_2$, and evolution of hydrogen ; and to prevent polarisation, the carbon plate is placed in a porous cell filled with fragments of carbon and powdered manganese dioxide, which slowly oxidises the hydrogen.

Silver Chloride Battery.—Warren de la Rue introduced a perfectly constant battery, in which zinc and silver are the two metals, and the electrolyte is formed of solid silver chloride. The zinc is immersed in a solution of sodium chloride or zinc chloride, and the silver, in the form of wire, is imbedded in a stick of fused silver chloride. As the zinc dissolves, silver is continually deposited on the wire, just as copper is deposited in the Daniell cells. The electromotive force of this battery is about equal to that of Daniell's. A battery of 11,000 of these cells gives a spark not quite a quarter of an inch long.

Secondary Batteries—Storage of Electric Energy.—In Grove's gas-battery, one form of which is shown in fig. 112, the platinum plates used for decomposing dilute sulphuric acid become charged with hydrogen and oxygen, liberated from the acid, the plate immersed in the hydrogen then acting like the zinc of an ordinary voltaic battery, and producing a current in a direction the reverse of that produced by the battery. In this way the power generated by a battery or other source of electricity may be stored up for use when required.

Fig. 112.



A more abundant storage of electric power may however be obtained by the electrolysis of a lead salt, whereby metallic lead is deposited on the cathode and dioxide of lead, PbO_2, on the anode; and when the plates thus coated are immersed in dilute sulphuric acid, the metallic lead becomes oxidised and the dioxide reduced, and a current is thereby developed, the positive electricity proceeding from the former to the latter, *i.e.*, in a direction opposite to that of the original current. If the plates are left unconnected, they may remain in the acid liquid for days without undergoing any change, or showing any signs of electric charge; but on connecting them by a wire, a current is immediately produced in the direction just indicated. Such is the principle of the secondary battery, invented by Planté, the plates of which consist of two pieces of sheet lead, rolled up together in cylindrical form, but not in metallic contact with each other. Its power may be greatly increased, as recommended by Faure, by covering the lead plates with a coating of red lead, an oxide intermediate between PbO and PbO_2. On passing a current through the cell, the red lead is peroxidised at the positive, and reduced at the negative electrode, first to a lower oxide, then to metallic lead. In this way a greater thickness of the working substance is obtained, and the time of charging is much shortened.

By means of these storage-batteries the power of an electric current generated in any way, by a dynamo-machine, for example, may be stored up and transported to any place at which it is required for use, as for working a railway, driving machinery, electro-plating,

electric lighting, &c. Faure's batteries are made with flat plates, arranged in a rectangular trough.

Electro-deposition of Metals.—*Experiment.*—A trough or cell divided by a porous diaphragm into two parts containing dilute sulphuric acid on one side, and a saturated solution of copper sulphate on the other. A plate of zinc is soldered to a wire or strip of copper, the other end of which is secured by similar means to an engraved copper plate or other work which it is desired to copy. If a plaster cast is used it must be carefully coated with graphite or bronze powder to give it a conducting surface. The plate is then immersed in the solution of copper and the zinc in the acid. To prevent deposition of copper on the back of the copper plate, that portion is covered with varnish. For small works, a porous earthenware cell, placed in a glass jar, may be used.

Other metals may be precipitated in the same manner, in a smooth and compact form, by the use of certain precautions which have been gathered by experience. In most operations upon a large scale the required current is now obtained most frequently by the use of some form of magneto-electric or dynamo-electric machine, driven by steam-power.

Experiment.—The production of the *lead-tree* (fig. 113) is dependent on electro-chemical action. When a piece of zinc is suspended in a solution of lead acetate the first effect is the decomposition of a portion of the latter, and the deposition of metallic lead upon the surface of the zinc; it is simply a displacement of a metal by a more oxidisable one. The change does not, however, stop here; metallic lead is still deposited in large and beautiful plates upon that first thrown down, until the solution becomes exhausted, or the zinc entirely disappears. The first portions of lead form with the zinc a voltaic arrangement by which the metal is precipitated upon the negative portion—that is, the lead—while the acid radicle is taken up by the zinc.

Fig. 113.

Crystallised metals, oxides, and other insoluble substances may be produced by the slow and continuous action of feeble electrical currents, kept up for months, or years. These products exactly resemble natural minerals: and their formation throws great light on the origin of the latter within the earth.

CHEMISTRY OF THE METALS.

THE metals constitute the second and larger group of elementary bodies. Many of them are of rare occurrence, being found only in a few scarce minerals; others are more abundant, and some few are almost universally diffused throughout the globe. Thus the larger portion of the solid earth is made up of aluminium and iron in the form of oxides and silicates, and calcium and magnesium in the form of carbonates. Potassium is tolerably abundant as a constituent of certain crystalline silicates. Sodium occurs in sea-water in salt deposits, and in smaller quantity in the soil as common salt. But the greater number of the other metals, with most of which we are familiar, such as lead, copper, zinc, tin, silver, gold, platinum, are found only locally and in comparatively small quantities.

The number of metals at present known is between fifty and sixty.

Physical Properties.—One of the most remarkable and striking characters possessed by the metals is their peculiar lustre; this is so characteristic, that the expression *metallic lustre* has passed into common speech. This property is no doubt connected with the great degree of opacity which all the metals present, the thinnest leaves or plates of these bodies, and the edges of crystalline laminæ, completely arresting the passage of light. An exception to this rule is exhibited by gold-leaf, which, when held up to day-light, exhibits a greenish colour, ard silver-leaf, which, when thin enough, shows a bluish transparency.

In point of *colour*, the metals present a certain degree of uniformity: with two exceptions—viz., copper and gold, which are yellowish-red—all these bodies are included between the pure white of silver and the bluish-grey tint of lead: bismuth, it is true, has a pinkish colour, and calcium and strontium a yellowish tint, but these tints are very feeble.

The differences of *density* are very wide, passing from lithium, potassium, and sodium, which are lighter than water, to platinum, which is more than twenty-one times heavier than an equal bulk of that liquid. (*See* table.)

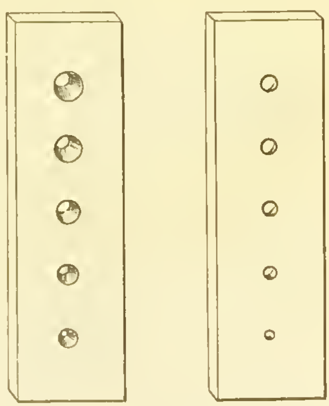
The density of malleable metals is usually very sensibly increased by pressure or blows, and the metals themselves are rendered much harder, with a tendency to brittleness. This condition is destroyed, and the former soft state restored by the operation of *annealing*, which consists in heating the metal to redness out of contact with air (if it will bear that temperature without fusion), and cooling it, quickly or slowly according to the circumstances of the case. After this operation, it is found to possess its original density.

The property of *malleability*, or power of extension under the hammer, or between the rollers of the flatting-mill, is possessed by

	Density.		Density.
Osmium, . .	22·48	Cadmium, . .	8·66
Iridium, . .	22·40	Molybdenum, .	8·63
Platinum, . .	21·50	Cobalt, . .	8·51
Gold, . .	19·265	Manganese, .	8·02
Uranium, . .	18·40	Iron, . . .	7·79
Tungsten, . .	18·30	Tin, . . .	7·29
Mercury, . .	13·60	Zinc, . . .	6·915
Rhodium, . .	12·1	Antimony, . .	6·72
Thallium, . .	11·8	Aluminium, .	2·67
Palladium, . .	11·4	Magnesium, .	1·74
Lead, . .	11·37	Calcium, . .	1·58
Silver, . .	10·47	Rubidium, . .	1·52
Bismuth, . .	9·82	Sodium, . .	0·97
Copper, . .	8·95	Potassium, . .	0·865
Nickel, . .	8·82	Lithium, . .	0·59

certain of the metals to a very great extent. Gold-leaf is a remarkable example of the tenuity to which a malleable metal may be brought by suitable means. The gilding on silver wire used in the manufacture of gold lace is even thinner, and yet presents an unbroken surface. Silver may be beaten out very thin,—copper also, but to an inferior extent; tin and platinum are easily rolled out into foil; iron, palladium, lead, nickel, cadmium, and metals of the alkalis, and mercury when solidified, are also malleable. Zinc may be placed midway between the malleable and brittle division; then perhaps bismuth; and, lastly, such metals as antimony, which are altogether destitute of malleability.

Fig. 114.



Ductility is a property distinct from the last, inasmuch as it involves the property of tenacity, or power of resisting tension. The art of wire-drawing is one of great antiquity; it consists in drawing rods of metal through a succession of conical holes in a steel plate (fig. 114), each being a little smaller than its predecessor, until the requisite degree of fineness is attained. The metal often becomes very hard and rigid in this process, and is then liable to break: this is remedied by annealing. The order of tenacity among the metals susceptible of being easily

drawn into wire is the following: it is determined by observing the weights required to break asunder wires drawn through the same orifice of the plate :—

Iron.	Silver.	Tin.
Copper.	Gold.	Lead.
Platinum.	Zinc.	

Metal differs as much in *fusibility* as in density. The following table will give an idea of their relations to temperature :—

		Melting points.
Fusible below a red heat.	Mercury,	−39·44°
	Gallium,	+30
	Rubidium,	+38·5
	Potassium,	62·5
	Sodium,	95·6
	Lithium,	180
	Tin,	235
	Bismuth,	270
	Thallium,	294
	Cadmium,	320
	Lead,	327
	Zinc,	433
	Antimony,	425
Infusible below a red heat.	Silver,	954
	Gold,	1037
	Copper,	1054
	Cast iron,	?
	Pure iron, Nickel, Cobalt, Manganese, Palladium,	Highest temperature of forge.
	Molybdenum, Uranium, Tungsten, Chromium,	Agglomerate, but do not melt in the forge.
	Titanium, Cerium, Osmium, Iridium, Rhodium, Platinum, Tantalum,	Infusible in ordinary blast-furnaces; fusible by oxy-hydrogen blow-pipe.

Some metals acquire a pasty or adhesive state before becoming fluid; this is the case with iron and platinum, and with the metals of the alkalis. It is this peculiarity which confers the very valuable property of welding, by which pieces of iron and steel are

united without solder, and the finely-divided metallic sponge of platinum is converted into a solid and compact bar.

Some metals are *volatile*, and this character would perhaps be exhibited by all, could sufficiently high temperatures be obtained. Mercury boils and distils below a red heat; potassium, sodium, zinc, magnesium, and calcium rise in vapour when heated to bright redness.

It has already been stated that metals generally are the best conductors of heat and electricity. In regard to their electric conductivity it has been found, as the result of recent experiments by Professor Fleming, that at low temperatures the conductivity of all pure metals is very much increased, or, in other words, their specific resistance is diminished. When the experimental results are plotted out, and curves drawn connecting the results of successive observations, the direction of these curves is such that if the absolute zero of temperature could be reached, they would all meet. This convergence indicates that *at the absolute zero the electrical resistance of all pure metals would vanish.* The resistance of a bad conductor—like lead, for example—is, therefore, diminished much more by cooling through a given range of temperature, than is the resistance of a good conductor like gold, silver, or copper. In some cases the order of conductivity is changed by cooling. At 13° pure silver is the best conductor, but at – 200° pure copper is better than silver.

The resistance of metallic alloys is reduced by cooling, but not at the same rate as the pure metals, and there is no sign of convergence of the curves representing their specific resistances. The determination of the resistance of a metal at the temperature of liquid air affords a delicate means of detecting impurities.

CHEMICAL RELATIONS OF THE METALS.

METALLIC combinations are of two kinds—namely, those formed by the union of metals among themselves, which are called *alloys*, or, where mercury is concerned, *amalgams*, and those generated by combination with the non-metallic elements, as oxides, chlorides, sulphides, etc. In this latter case, the metallic characters are invariably lost.

Alloys.—Most metals are probably, to some extent, capable of existing in a state of combination with each other in definite proportions; but it is difficult to obtain these compounds in the separate state, since they dissolve in all proportions in the melted metals, and do not generally differ so widely in their melting points from the metals they may be mixed with, as to be separated by crystallisation in a definite form. Exceptions to this rule are met with in the cooling of argentiferous lead, and in the crystallisation of brass and of gun-metal.

The affinity manifested between different metals is for the most part very feeble, and in all cases of combination between metals, the alteration of physical characters, which is one distinctive feature of chemical combination, does not take place to any great extent. The most unquestionable compounds of metals with metals are still metallic in their general physical characters, and there is no such transmutation of the individuality of their constituents as takes place in the combination of a metal with oxygen, sulphur, chlorine, etc. The alteration of characters in alloys is generally limited to the colour, degree of hardness, tenacity, or electric conductivity, and it is only when the constituent metals are capable of assuming opposite chemical relations that these compounds are distinguished by great brittleness. Chemical action is indicated in some cases, when two metals are melted together by such phenomena as the evolution of heat, as in the case of platinum and tin, copper and zinc, etc.

The density of alloys differs from that of mere mixtures of the metals. In the solidification of alloys, the temperature does not always fall uniformly, but often remains stationary at particular degrees, which may be regarded as the solidifying points of the compounds then crystallising. Tin and lead melted together in the proportion of about 2 parts of tin to 1 part of lead form a compound which solidifies at 180°. The melting point of an alloy is often very different from the point of solidification, and it is generally lower than the mean melting point of the constituent metals.

The chemical action of reagents upon alloys is sometimes very different from their action upon metals in the separate state: thus, platinum alloyed with silver is readily dissolved by nitric acid, but

is not affected by that acid when unalloyed. On the contrary, silver, which in the separate state is readily dissolved by nitric acid, is not dissolved by it when alloyed with gold in proportions much more than one-fourth of the alloy by weight.

Compounds of Metals with Non-Metals—Classification of Metals.

A classification of the metals and metalloids according to their valency is given in the table on page 268. There are, however, several metals, especially among those of rare occurrence, whose position in the series is by no means definitely fixed; and partly on this account, partly because metals of equal valency or combining capacity do not, as a rule, resemble one another in their physical and chemical characters so closely as non-metallic elements of equal combining capacity (*e.g.*, Cl, Br, I, and S, Se, Te, etc.), it is preferable, in describing the metals and semi-metals or metalloids, to classify them according to their general agreement in physical and chemical properties rather than in strict accordance with their valency.

The following arrangement based upon this principle does not, however, deviate greatly from the order of valency :—

1. METALS OF THE ALKALIS :—
   Potassium—Sodium—Lithium—Rubidium—Cæsium.
2. METALS OF THE ALKALINE EARTHS :—
   Calcium—Strontium—Barium.
3. MAGNESIUM GROUP :—
   Beryllium—Magnesium—Zinc—Cadmium.
4. MERCURY :—
5. LEAD GROUP :—
   Thallium—Lead.
6. COPPER GROUP :—
   Copper—Silver.
7. YTTRIUM GROUP :—
   Scandium—Yttrium—Erbium—Terbium—Ytterbium—Lanthanum—Cerium—Didymium.
8. ALUMINIUM GROUP :—
   Aluminium—Gallium—Indium.
9. IRON GROUP :—
   Manganese—Iron—Cobalt—Nickel.
10. CHROMIUM GROUP :—
    Chromium—Molybdenum—Tungsten—Uranium.

11. Tin Group :—

Germanium—Tin—Titanium—Zirconium—Thorium.

12. Antimony Group :—

Antimony—Bismuth—Vanadium—Niobium—Tantalum.

13. Platinum Group :—

Gold—Platinum — Iridium — Osmium — Palladium — Rhodium—Ruthenium.

The degrees of combining capacity of the metals in these several groups are for the most part less easy to determine than those of the non-metallic elements. All the latter unite with hydrogen, forming volatile compounds, the vapour-densities of which are easily determined, and afford trustworthy data for fixing the molecular weight and constitution of these compounds. Hydrogen silicide, for example, has a vapour-density of 16 : consequently its molecular weight is 32, and, as analysis shows the compound to contain 7 parts by weight of silicon to 1 part of hydrogen, its molecule must contain 28 parts Si and 4H, and its molecular formula must be SiH_4, showing that silicon is a tetrad. But with the metals this mode of proceeding is not available : for only one of them, viz., antimony, forms a volatile compound with hydrogen ; and if we endeavour to fix the valence of a metal by its mode of combination with chlorine or other univalent element, we find that the results are not always accordant. Thus molybdenum and tungsten form pentachlorides, whence it might be inferred that they are pentads : but tungsten also forms a hexchloride, and both these metals, in their oxygen-compounds, exhibit so marked an analogy to sulphur, that they must be regarded as hexads.

Moreover, we have in many cases no means of ensuring that the formulæ assigned to these several chlorides actually represent the molecules : for the only trustworthy method of determining the weight of a molecule of a salt is by means of its vapour-density, and in the case of a great number of metallic chlorides (also bromides and iodides), this determination cannot be satisfactorily made, on account of the very high temperatures required to volatilise them.

In many cases indeed it seems probable that the molecular constitution of metallic chlorides, bromides, &c., should be represented, not by formulæ containing single atoms of the respective metals like those above given, but by multiples thereof,—potassium chloride, for example, by the double formula $K_2\ Cl_2$, into which either the metal or the halogen enters as a diad or triad, according to the manner in which we may imagine their atoms to be linked together.

$$\begin{array}{ccccc} \mathrm{Cl{-}K{-}K{-}Cl} & & \mathrm{Cl{-}K} & & \mathrm{K{-}Cl{-}Cl{-}K} \\ \quad | \quad\ | & \text{or} & \| \quad \| & \text{or} & \quad | \quad\ | \\ \mathrm{Cl{-}K{-}K{-}Cl} & & \mathrm{Cl{-}K} & & \mathrm{K{-}Cl{-}Cl{-}K} \end{array} \text{, \&c.}$$

For since potassium and chlorine are easily volatile bodies, the chloride, if correctly represented by the simple formula KCl, might

be expected to volatilise at a comparatively low temperature, lower, for example, than the temperatures required to volatilise the more complex molecules $HgCl_2$ and $SbCl_3$, whereas it actually requires a strong red heat to convert it into vapour; and similar remarks might be made with regard to many other haloid salts of the metals. In stating, therefore, that potassium chloride is represented by the formula KCl, and calcium chloride by $CaCl_2$, all that we mean to say is that for every atom of metal in these compounds, the first contains one atom of chlorine, and the second two atoms; and in this sense — whatever may be the number of atoms contained in the molecule—potassium is certainly univalent, or equivalent to one atom of hydrogen, and calcium bivalent, or equivalent to two atoms of hydrogen.

The metals of the alkalis and alkaline earths, on account of their inferior density, are often called light metals; the others, heavy metals.

Metallic Chlorides.—All metals combine with chlorine, and most of them in several proportions, as above indicated, forming compounds which may be regarded as derived from one or more molecules of hydrogen chloride, by substitution of a metal for an equivalent quantity of hydrogen; thus:—

From	HCl	are derived	monochlorides	like	KCl
„	H_2Cl_2	„	dichlorides	„	$BaCl_2$
„	H_3Cl_3	„	trichlorides	„	$AuCl_3$
„	H_4Cl_4	„	tetrachlorides	„	$SnCl_4$, &c., &c.

Hydrochloric acid may, in fact, be regarded as the type of chlorides in general.

Several chlorides occur as natural products. Sodium chloride, or common salt, occurs in enormous quantities, both in the solid state as rock-salt, and dissolved in sea-water, and in the water of rivers and springs. Potassium chloride occurs in the same forms, but in smaller quantity; the chlorides of lithium, cæsium, rubidium, and thallium also occur in small quantities in certain spring waters. Mercurous chloride, Hg_2Cl_2 and silver chloride, AgCl, occur as natural minerals.

1. Chlorides are generally prepared by one or other of the following processes: (1) By acting upon the metal with chlorine gas. Antimony pentachloride and copper dichloride, are examples of chlorides sometimes produced in this manner. The chlorides of gold and platinum are usually prepared by acting upon the metals with nascent chlorine, developed by a mixture of hydrochloric and nitric acids. Sometimes, on the other hand, the metal is in the nascent state, as when titanic chloride is formed by a passing current of chlorine over a heated mixture of charcoal and titanic oxide. The chlorides of aluminium and chromium may be obtained by similar processes.

2. Chlorine gas, by its action upon metallic oxides, drives out the oxygen, and unites with the respective metals to form chlorides. This reaction sometimes takes place at ordinary temperatures, as is the case with silver oxide; sometimes only at a red heat, as is the case with the oxides of the alkali-metals and alkaline earth-metals. The hydroxides and carbonates of these last metals, when dissolved or suspended in hot water and treated with excess of chlorine, are converted, chiefly into chlorides, partly into chlorates.

3. Many metallic chlorides are prepared by acting upon the metals with hydrochloric acid. Zinc, cadmium, iron, nickel, cobalt, and tin dissolve readily in hydrochloric acid, with liberation of hydrogen; copper only in the strong boiling acid; silver, mercury, palladium, platinum, and gold, not at all. Sometimes the metal is substituted, not for hydrogen, but for some other metal. Stannous chloride, for instance, may be made by distilling metallic tin with mercuric chloride; thus: $HgCl_2 + Sn = SnCl_2 + Hg$.

4. By dissolving a metallic oxide, hydroxide, or carbonate in hydrochloric acid.

All monochlorides and dichlorides are soluble in water excepting silver chloride, $AgCl$, and mercurous chloride, Hg_2Cl_2; lead chloride, $PbCl_2$, is sparingly soluble; these three chlorides are easily formed by precipitation. Many metallic chlorides dissolve also in alcohol and in ether.

Most monochlorides, dichlorides, and trichlorides volatilise at high temperatures without decomposition; the higher chlorides when heated give off part of their chlorine. Some chlorides which resist the action of heat alone are decomposed by ignition in the air, yielding metallic oxides and free chlorine; this is the case with the dichlorides of iron and manganese; but most dichlorides remain undecomposed, even in this case. All metallic chlorides, excepting those of the alkali-metals and earth-metals, are decomposed at a red heat by hydrogen gas, with formation of hydrogen chloride: in this way metallic iron may be obtained in fine cubical crystals. Silver chloride, placed in contact with metallic zinc or iron, under dilute sulphuric or hydrochloric acid, is reduced to the metallic state by the nascent hydrogen.

Sulphuric, phosphoric, boric, and arsenic acids decompose most metallic chlorides, sometimes at ordinary, sometimes at higher temperatures. Nearly all metallic chlorides, heated with lead dioxide or manganese dioxide and sulphuric acid, give off chlorine, *e.g.*:

$$2NaCl + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2.$$

Chlorides distilled with sulphuric acid and potassium chromate, yield a dark red liquid distillate of chromic oxychloride. Some metallic chlorides are decomposed by *water*, forming hydrochloric acid and an oxychloride, *e.g.*: $BiCl_3 + H_2O = 2HCl + BiClO$. The chlorides of antimony and stannous chloride are decomposed in a similar manner.

All soluble chlorides give with solution of *silver nitrate* a white

precipitate of silver chloride, easily soluble in ammonia, insoluble in nitric acid. With *mercurous nitrate*, they yield a white curdy precipitate of mercurous chloride, blackened by ammonia; and with *lead-salts*, not too dilute, a white precipitate of lead chloride, soluble in excess of water.

Metallic chlorides unite with each other and with the chlorides of the non-metallic elements, forming such compounds as potassium mercuro-chloride, $2KCl.HgCl_2$, sodium platino-chloride, $2NaCl.PtCl_4$, potassium iodo-perchloride, $KCl.ICl_3$, etc. Metallic chlorides combine in definite proportions with ammonia and organic bases: the chlorides of platinum form with ammonia the compounds $2NH_3$ $PtCl_2$, $4NH_3.PtCl_2$, $2NH_3.PtCl_4$, and $4NH_3.PtCl_4$; mercuric chloride forms with aniline the compound $3C_6H_7N.HgCl_2$, etc.

Chlorides also unite with oxides and sulphides, forming *oxychlorides* and *thio-chlorides*, which may be regarded as chlorides having part of their chlorine replaced by an equivalent quantity of oxygen or sulphur (Cl_2 by O or S). Bismuth, for example, forms an oxychloride having the composition $BiClO$ or $BiCl_3,Bi_2O_3$.

Bromides.—Bromine unites directly with most metals, forming compounds analogous in composition to the chlorides, and resembling them in most of their properties. The bromides of the alkali-metals occur in sea-water and in many saline springs; silver bromide occurs as a natural mineral. Nearly all bromides are soluble in water, and may be formed by treating an oxide, hydroxide, or carbonate with hydrobromic acid, the solutions when evaporated giving off water for the most part, and leaving a solid metallic bromide; some of them, however, namely, the bromides of magnesium, aluminium, and the other earth-metals, are more or less decomposed by evaporation, giving off hydrobromic acid, and leaving a mixture of metallic bromide and oxide. Silver bromide and mercurous bromide are insoluble in water, and lead bromide is very sparingly soluble; these are obtained by precipitation.

Metallic bromides are solid at ordinary temperatures; most of them fuse at a moderate heat, and volatilise at higher temperatures. The bromides of gold and platinum are decomposed by mere exposure to heat; many others give up their bromine when heated in contact with the air. *Chlorine*, with the aid of heat, drives out the bromine and converts them into chlorides. *Hydrochloric acid* also decomposes them at a red heat, giving off hydrobromic acid. Strong *sulphuric* or *nitric acid* decomposes them, with evolution of hydrobromic acid, which, if the sulphuric or nitric acid is concentrated, and in excess, is partly decomposed, with separation of bromine and formation of sulphurous oxide or nitric oxide. Bromides heated with *sulphuric acid* and *manganese dioxide* or *potassium chromate*, give off free bromine.

Bromides in solution are easily decomposed by chlorine, either in the form of gas or dissolved in water, the liquid acquiring a red or reddish-yellow colour, according to the quantity of bromine present;

and on agitating the liquid with ether, that liquid dissolves the bromine, forming a red solution, which rises to the surface.

Soluble bromides give with *silver nitrate* a white precipitate of silver bromide, greatly resembling the chloride, but much less soluble in ammonia, insoluble in hot nitric acid. *Mercurous nitrate* produces a yellowish-white precipitate ; and *lead acetate* a white precipitate much less soluble in water than the chloride.

Bromides unite with each other in the same manner as chlorides ; also with oxides, sulphides, and ammonia.

Iodides.—These compounds are obtained by processes similar to those which yield the chlorides and bromides. Many metals unite directly with iodine. Potassium and sodium iodides exist in sea-water and in many salt springs ; silver iodide occurs as a natural mineral.

Metallic iodides are analogous to the bromides and chlorides in composition and properties. But few of them are decomposed by heat alone ; the iodides of gold, silver, platinum, and palladium, however, give up their iodine when heated.

Most metallic iodides are perfectly soluble in water ; but lead iodide is very slightly soluble, and the iodides of mercury and silver and cuprous iodide are quite insoluble.

Solutions of iodides evaporated out of contact of air, generally leave anhydrous metallic iodides, which partly separate in the crystalline form before the water is wholly driven off. The iodides of the earth-metals, however, are resolved, on evaporation, into the earthy oxides and hydriodic acid, which escapes. A very small quantity of *chlorine* colours the solution yellow or brown, by partial decomposition ; and a somewhat larger quantity takes up the whole of the metal, forming a chloride, and separates the iodine, which then gives a blue colour with starch ; a still larger quantity of chlorine gives the liquid a paler colour, and converts the separated iodine into trichloride of iodine, which does not give a blue colour with starch, and frequently enters into combination with a metallic chloride produced. Strong *sulphuric acid* and somewhat concentrated *nitric acid* colour the solution yellow or brown ; and if the quantity of the iodide is large, and the solution much concentrated or heated, the liberated iodine partly escapes in violet vapours.

The aqueous solution of an iodide gives a brown precipitate with salts of *bismuth* ; golden-yellow with *lead* salts ; dirty-white with *cuprous* salts, also with *cupric* salts, at the same time liberating iodine ; greenish-yellow with *mercurous* salts ; scarlet with *mercuric* salts ; pale yellow with *silver* salts ; brown with *platinic* salts—first, however, turning the liquid dark brown-red ; and black with salts of *palladium*, even when extremely dilute. All these precipitates consist of metallic iodides : the silver precipitate is insoluble in nitric acid and very little soluble in ammonia.

Metallic iodides unite with one another, forming double iodides, corresponding to the double chlorides ; they also absorb ammonia gas in definite proportions.

Fluorides.—These compounds are formed—(1) By heating hydrofluoric acid with certain metals. (2) By the action of that acid on metallic oxides. (3) By displacement of one metal by another as in formation of fluoride of lead or fluoride of mercury. (4) Volatile metallic fluorides may be prepared by heating fluor-spar with sulphuric acid and the oxide of the metal.

Fluorides are usually fusible, and for the most part resemble the chlorides. They are not decomposed by ignition, either alone or when mixed with charcoal. When ignited in contact with the air, in a flame which contains aqueous vapour, many of them are converted into oxides, while the fluorine is given off as hydrofluoric acid. They are decomposed at a gentle heat by strong *sulphuric acid*, with formation of metallic sulphate and evolution of hydrofluoric acid.

The fluorides of ammonium, potassium, sodium, and silver are easily soluble in water. The rest are for the most part insoluble. The solutions of ammonium, potassium, and sodium fluorides have an alkaline reaction. The aqueous solutions of fluorides corrode glass vessels in which they are kept or evaporated. They form with soluble *calcium salts* a precipitate of calcium fluoride, in the form of a transparent jelly, which is scarcely visible, because its refractive power is nearly the same as that of the liquid ; the addition of ammonia makes it plainer. This precipitate, if it does not contain silica, dissolves with some difficulty in hydrochloric or nitric acid, and is re-precipitated by ammonia. The aqueous fluorides give a pulverulent precipitate with lead acetate.

The fluorides of antimony, arsenic, chromium, mercury, niobium, osmium, tantalum, tin, titanium, tungsten, and zinc are volatile without decomposition.

Fluorine has a great tendency to form double salts, consisting of a fluoride of a basic or positive metal united with the fluoride of hydrogen, boron, silicon, tin, titanium, zirconium, &c., *e.g.* :

Potassium hydrofluoride, . . .	KHF_2	$= KF,HF$
Potassium borofluoride, . . .	KBF_4	$= KF,BF_3$
Potassium silicofluoride, . . .	K_2SiF_6	$= 2KF,SiF_4$
Potassium titanofluoride, . .	K_2TiF_6	$= 2KF,TiF_4$
Potassium stannofluoride, . .	K_2SnF_6	$= 2KF,SnF_4$
Potassium zircofluoride, . . .	K_2ZrF_6	$= 2KF,ZrF_4$

Cyanides.—Closely related to these haloïd compounds are the cyanides, formed by the union of metals with the group CN, cyanogen, CN.

Some metals—potassium among the number—are converted into cyanides by heating them in cyanogen gas or vapour of hydrocyanic acid. The cyanides of the alkali-metals are also formed (together with cyanates) by passing cyanogen gas over the heated hydroxides or carbonates of the same metals ; potassium cyanide also, by passing nitrogen gas over a mixture of charcoal and hydroxide or carbonate

of potassium at a bright red heat. Cyanides are formed abundantly when nitrogenous organic compounds are heated with fixed alkalis.

The cyanides of the alkali-metals, and of barium, strontium, calcium, magnesium, and mercury, are soluble in water, and may be produced by treating the corresponding oxides or hydroxides with hydrocyanic acid. Nearly all other metallic cyanides are insoluble, and are obtained by precipitation from the soluble cyanides.

The cyanides of the alkali-metals sustain a red heat without decomposition, provided air and moisture be excluded. The cyanides of many of the heavy metals, as lead, iron, cobalt, nickel, and copper, at a red heat, give off all their nitrogen as gas, and leave a metallic carbide; mercuric and silver cyanides are resolved into the metal, paracyanogen and cyanogen gas. Most cyanides, when heated with dilute acids, give off hydrocyanic acid.

Cyanides have a strong tendency to unite with one another, forming double cyanides. The most important of these are the double cyanides of iron and potassium, namely, *potassium ferro-cyanide*, $4KCN.Fe(CN)_2$ or rather $K_4(FeC_6N_6)$, commonly called yellow prussiate of potash ; and *potassium ferri-cyanide*, $3KCN.Fe(CN)_3$ or rather $K_3(FeC_6N_6)$, commonly called red prussiate of potash. Both these are splendidly crystalline salts, which dissolve easily in water, and formed highly characteristic precipitates with many metallic salts.

Oxides.—All metals combine with oxygen, and most of them in several proportions. In almost all cases oxides are formed corresponding in composition with the chlorides, one atom of oxygen taking the place of two atoms of chlorine. Many metals also form oxides to which no chlorine analogues are known ; thus barium which forms only one chloride, $BaCl_2$, forms, in addition to the monoxide, BaO, a dioxide, BaO_2, osmium also, the highest chloride of which is $OsCl_4$, forms, in addition to the dioxide, a trioxide and a tetroxide.

Just as chlorides may be supposed to be derived by substitution from hydrochloric acid, HCl, so likewise may oxides be derived from one or more molecules of water, H_2O ; but as the molecule of water contains two hydrogen-atoms the replacement of the hydrogen may, as already explained, be either total or partial, the product in the first case being an anhydrous metallic oxide, and in the second a hydrated oxide or hydroxide, in which the oxygen is associated both with hydrogen and with metal; in this manner the following hydroxides and anhydrous oxides may be constituted :—

Hydroxides.	Oxides.
KHO	K_2O
BaH_2O_2	BaO
BiH_3O_3	Bi_2O_3
ZrH_4O_4	ZrO_2

It may be observed that the hydroxides of bi- or quadrivalent

metals contain the elements of a molecule of the corresponding anhydrous oxide, and of one or more molecules of water, and may therefore also be regarded as hydrates; thus—

Barium hydroxide or hydrate,	.	$BaH_2O_2 = BaO,H_2O$
Stannic „ „	.	$SnH_2O_3 = SnO_2,H_2O$
Zirconium „ „	.	$ZrH_4O_4 = ZrO_2,2H_2O$.

But the hydroxide of a perissad metal contains in its molecule only half the number of atoms required to make up a molecule of oxide together with a molecule of water; thus—

Potassium hydroxide, . . . $KHO = \frac{1}{2}(K_2O,H_2O)$.

Many metallic oxides occur as natural minerals, and some, especially those of iron, tin, and copper, in large quantities, forming ores from which the metals are extracted.

All metals, except gold, platinum, iridium, and rhodium, are capable of uniting directly with oxygen. Some, as potassium, sodium, and barium, oxidise rapidly on exposure to the air at ordinary temperatures, and decompose water with energy. Most metals, however, when in the massive state, remain perfectly bright and unacted on in dry air or oxygen gas, but oxidise slowly when moisture is present; such is the case with iron, zinc, and lead. Some of the ordinarily permanent metals, when in a very finely divided state, as lead when obtained by ignition of its tartrate, and iron reduced from its oxide by ignition in hydrogen gas, oxidise spontaneously and take fire as soon as they come in contact with the air. Lead, iron, copper, and the volatile metals, antimony, zinc, cadmium, and mercury, are converted into oxide when heated in air or oxygen. Many metals, especially at a red heat, are readily oxidised by water or steam. A very general method of preparing metallic oxides is to subject the corresponding hydroxides, carbonates, or nitrates, to the action of heat.

Oxides are for the most part opaque earthy bodies, destitute of metallic lustre. The majority of them are fusible, though at temperatures above the melting points of the uncombined metals; those of lead and bismuth at a low red heat; those of copper and iron at a white heat; those of barium and aluminium before the oxyhydrogen blow-pipe; while calcium oxide or lime fuses only at the temperature of the electric arc. Osmium tetroxide and antimonious oxide are volatile.

A greater or lesser degree of heat effects the decomposition of many metallic oxides. Those of gold, platinum, silver, and mercury are reduced to the metallic or reguline state by an incipient red heat. At a somewhat higher temperature, the higher oxides of barium, cobalt, nickel, and lead are reduced to the state of monoxides; while the trimetallic tetroxides of manganese and iron, Mn_3O_4 and Fe_3O_4, are produced by exposing manganese dioxide, MnO_2, and iron sesquioxide, Fe_2O_3, respectively to a still stronger heat. By gentle ignition,

arsenic and antimonic oxides are reduced to arsenious and antimonious oxides, and chromium trioxide to sesquioxide.

The superior oxides of the metals are easily reduced to a lower state of oxidation by the action of a current of *hydrogen gas* at a more or less elevated temperature. At a higher temperature, hydrogen gas will transform to the reguline state all metallic oxides except the sesquioxides of aluminium and chromium, and the monoxides of manganese, magnesium, barium, strontium, calcium, lithium, sodium, and potassium. The temperature necessary to enable hydrogen to effect the decomposition of some oxides is comparatively low. Thus metallic iron may be reduced from its oxides by hydrogen gas at a heat considerably below redness. *Carbon*, at a red or white heat, is a still more powerful deoxidising agent than hydrogen, and seems to be capable of completely reducing all metallic oxides whatsoever. The oxidisable metals in general act as reducing agents.

Chlorine decomposes all metallic oxides, except those of the earth-metals (aluminium, &c.), converting them into chlorides, and expelling the oxygen. With silver oxide this reaction takes place at ordinary temperatures; with the alkalis and alkaline earths, at a full red heat. *Sulphur*, at high temperatures, can decompose most metallic oxides; with many oxides—those of silver, mercury, lead, and copper, for instance—metallic sulphides and sulphur dioxide are produced; with the highly basylous oxides, the products are metallic sulphate and sulphide. There are some oxides upon which sulphur exerts no action. Of these the principal are magnesia, alumina, chromic, stannic, and titanic oxides. By boiling sulphur with soluble hydroxides, mixtures of polysulphide and thiosulphate are produced. With the exception of magnesia, alumina, and chromic oxide, most metallic oxides can absorb sulphuretted hydrogen, to form metallic sulphide or hydrosulphide and water.

Oxygen-salts or **Oxysalts.**—Oxides may be divided into three classes, *acidulous*, *neutral*, and *basylous*, the first and third being capable of uniting with one another in definite proportions, and forming compounds called salts. The most characteristic of the acid-forming oxides are those of certain non-metals, as nitrogen, sulphur, and phosphorus, which unite readily with water or the elements of water, forming compounds called oxygen-acids, distinguished by sour taste, solubility in water, and the power of reddening certain vegetable blue colours. The most characteristic of the basylous oxides, on the other hand, are those of the alkali-metals and alkaline earth-metals, which likewise dissolve in water, but form alkaline solutions possessing in an eminent degree the power of *neutralising* acids and forming salts with them. The same power is exhibited more or less by the monoxides of most other metals, as zinc, iron, copper, manganese, &c., and by the sesquioxides of aluminium, iron, chromium, and others. The higher oxides of several of these metals—the trioxides of chromium, for example—exhibit acid characters, being capable of forming salts with the

more basic oxides; and some metals, as niobium and tantalum, form only acidulous oxides.

In some cases salts are formed by the direct combination of an acid and a basic oxide. Thus, when vapour of sulphuric oxide, SO_3, is passed over barium oxide, BaO, the two combine together, and form barium sulphate, BaO,SO_3 or $BaSO_4$. Silicic oxide, SiO_2, phosphoric oxide, P_4O_{10}, boric oxide, B_2O_3, and other acid oxides capable of withstanding a high temperature without decomposing or volatilising, likewise unite with basic oxides when heated with them, and form salts.

But in the majority of cases metallic salts are formed by substitution, or interchange of a metal for hydrogen, or of one metal for another. It is clear, indeed, that any metallic salt (zinc sulphate, ZnO,SO_3, for example) may be derived from the corresponding acid or hydrogen salt (H_2O,SO_3) by substitution of a metal for an equivalent quantity of hydrogen. Accordingly, metallic salts are frequently produced by the action of an acid on a metal or a metallic oxide or hydroxide, thus—

$$
\begin{array}{lllll}
(1) & H_2SO_4 + Zn & = ZnSO_4 & + H_2. \\
(2) & 2HNO_3 + Ag_2O & = 2AgNO_3 & + H_2O. \\
(3) & HNO_3 + KHO & = KNO_3 & + H_2O.
\end{array}
$$

In the instances represented by these equations, the metallic salts formed are soluble in water. Insoluble salts are frequently prepared by interchange of the metals between two soluble salts, barium nitrate and sodium sulphate, for example, thus—

$$(4) \quad Ba(NO_3)_2 + Na_2SO_4 = BaSO_4 + 2NaNO_3.$$

In this case the barium sulphate, being insoluble, is precipitated, while the sodium nitrate remains in solution.

In all these reactions, hydrochloric acid or a metallic chloride might be substituted for the oxygen-acid or oxygen-salt, without the slightest alteration in the mode of action, the product formed in each case being a chloride instead of a nitrate or sulphate; thus:—

$$
\begin{array}{llllllll}
(1') & 2HCl & + & Zn & = & ZnCl_2 & + & H_2 \\
(2') & 2HCl & + & Ag_2O & = & 2AgCl & + & H_2O \\
(3') & HCl & + & KHO & = & KCl & + & H_2O \\
(4') & AgNO_3 & + & NaCl & = & AgCl & + & NaNO_3.
\end{array}
$$

From all these considerations it appears that oxygen-salts may be regarded, either as compounds of acid oxides with basic oxides, or as analogous in composition to chlorides,—that is to say, as compounds of a metal with a radicle or group of elements, such as NO_3 (*nitrion*) in the nitrates, SO_4 (*sulphion*) in the sulphates, discharging functions similar to those of chlorine, and capable, like that element, of passing unchanged from one compound to another.

For many years, indeed, it was a subject of discussion among chemists, whether the former or the latter of these views should be

regarded as representing the *actual* constitution of oxygen salts. Berzelius divided salts into two classes: (1) Haloïd salts comprising, as already mentioned, the chlorides, bromides, iodides, and fluorides, which are compounds of a metal with a monad metallic element.—(2) Amphid salts, consisting of an acid or electro-negative oxide, sulphide, selenide, or telluride, with a basic or electro-positive compound of the same kind; such as potassium arsenate, $3K_2O,As_2O_5$; potassium sulpharsenate, $3K_2S,As_2S_5$; potassium seleniophosphate, $2K_2Se,P_2Se_5$, &c.

Davy, however, observing the close analogy between the reactions of chlorides, on the one hand, and of oxygen-salts, such as sulphates, nitrates, &c., on the other, suggested that the latter might be regarded, like the former, as compounds of metals with acid or electro-negative radicles, the only difference being, that in the former the acid radicle is an elementary body, Cl, Br, &c., whereas in the former it is a compound, as SO_4, NO_3, PO_4, &c. This was called the *binary theory of salts*; it was supported by many ingenious arguments by its proposer and several contemporary chemists; in later years also by Liebig, and by Daniell and Miller, who observed that the mode of decomposition of salts by the electric current is more easily represented by this theory than by the older one.

The formulæ now in use are intended to exhibit, first, the balance of neutralisation of the units of valency or combining capacity of the several elements contained in a compound; and, secondly, the manner in which any compound or group of atoms tends to split up into subordinate groups under the influence of different reagents.

Examples of constitutional formulæ have already been given (p. 262).

Basicity of Acids.—Normal, Acid, and Double Salts.—Acids are monobasic, bibasic, tribasic, &c., according as they contain one or more atoms of hydrogen replaceable by metals; thus nitric acid, HNO_3, and hydrochloric acid, HCl, are monobasic; sulphuric acid, H_2SO_4, is bibasic; phosphoric acid, H_3PO_4, is tribasic.

Monobasic acids form but one class of salts by substitution, the metal taking the place of the hydrogen in one, two, or three molecules of the acid, according to its equivalent value: thus the action of hydrochloric acid on sodium, zinc, and aluminium is represented by the equations:

$$\begin{array}{lclclcl} HCl & + & Na & = & NaCl & + & H \\ 2HCl & + & Zn & = & ZnCl_2 & + & H_2 \\ 3HCl & + & Al & = & AlCl_3 & + & H_3, \end{array}$$

and that of nitric acid on the hydroxides of the same metals by the equations:

$$\begin{array}{lclclcl} HNO_3 & + & Na(HO) & = & NaNO_3 & + & H(HO) \\ 2HNO_3 & + & Ba(HO)_2 & = & Ba(NO_3)_2 & + & 2H(HO) \\ 3HNO_3 & + & Al(HO)_3 & = & Al(NO_3)_3 & + & 3H(HO). \end{array}$$

Bibasic acids, on the other hand, form two classes of salts, viz., *primary* or *acid salts*, in which half the hydrogen is replaced by a metal; and *secondary salts*, in which the whole of the hydrogen is thus replaced, the salt being called *normal* or *neutral* if it contains one metal, and *double* if it contains two metals, thus:

From H_2SO_4	is derived	$KHSO_4$	potassium hydrogen sulphate, primary, or acid potassium sulphate.
„ „	„	K_2SO_4	dipotassium sulphate, secondary, or normal sulphate.
„ H_2SO_4	„	$BaSO_4$	barium sulphate.
„ $2H_2SO_4$	„	$NaK_3(SO_4)_2$	sodium tripotassium sulphate.
„ „	„	$KAl(SO_4)_2$	potassium aluminium sulphate.
„ $3H_2SO_4$	„	$Al_2(SO_4)_3$	normal aluminium sulphate.

Tribasic acids in like manner form two classes of acid salts, *primary* or *secondary*, according as one-third or two-thirds of the hydrogen is replaced by a *metal*: also *tertiary salts*, including *normal* and *double* or *triple salts*, in which the hydrogen is wholly replaced by one or more metals; in quadribasic acids the variety is, of course, still greater.

The use of the terminations *ous* and *ic*, as applied to salts, has already been explained. We have only further to observe in this place that when a metal forms but one class of salts, it is for the most part better to designate those salts by the name of the metal itself than by an adjective ending in *ic*; thus *potassium nitrate*, and *lead sulphate*, are mostly to be preferred to *potassic nitrate* and *plumbic sulphate*. But in naming double salts, and in many cases where a numeral prefix is required, the names ending in *ic* are more euphonious; thus *triplumbic phosphate* sounds better than *trilead phosphate*, but there is no occasion for a rigid adherence to either system.

All oxygen-salts may also be represented as compounds of an acid oxide, with one or more molecules of the same or different basic oxides, including water, *e.g.*:—

Hydro-potassic sulphate,	$2HK(SO_4)$	=	$H_2O,K_2O,2SO_3$
Sodio-tripotassic sulphate,	$2NaK_3(SO_4)_2$	=	$Na_2O,3K_2O,4SO_3$
Potassio-aluminic sulphate,	$2KAl(SO_4)_2$	=	$K_2O,Al_2O_3,4SO_3$.
Hydrodisodic phosphate,	$2HNa_2(PO)_4$	=	$H_2O,2Na_2O,P_2O_5$.

When a normal oxygen-salt is thus formulated, it is easy to see that the number of molecules of acid oxide contained in its molecule is equal to the number of oxygen-atoms in the base; thus:

Normal potassium sulphate,	K_2SO_4	=	K_2O,SO_3
„ barium sulphate,	$BaSO_4$	=	BaO,SO_3
„ stannic sulphate,	$Sn(SO_4)_2$	=	$SnO_2,2SO_3$
„ aluminium sulphate,	$Al_2(SO_4)_3$	=	$Al_2O_3,3SO_3$.

When the proportion of acid oxide is less than this, the salt is

called basic ; such salts may be regarded as compounds of a normal salt with one or more molecules of basic oxide, or as derived from normal salts by substitution of oxygen for an equivalent quantity of the acid radicle ; thus :

$$\begin{array}{lll} \text{Tribasic lead nitrate,} & 3PbO,N_2O_5 & = Pb(NO_3)_2,2PbO \\ & & = Pb_3(NO_3)_2O_2 \\ \left.\begin{array}{l}\text{Quidribasic alumi-} \\ \text{nium sulphate,}\end{array}\right\} & 4Al_2O_3,3SO_3 & = 3Al_2O_3Al_2(SO_4)_3 \\ & & = Al_8(SO_4)_3O_9 . \end{array}$$

The last mode of formulation exhibits the analogy of these basic oxysalts to the oxychlorides, oxyiodides, etc. ; thus the basic lead nitrate, $Pb_3(O_3)_2O_2$, just mentioned, is analogous to the oxychloride of that metal, $Pb_3Cl_2O_2$, which occurs native as mendipite.

The constitutional formulæ of such compounds would represent them as containing atoms of metal linked together by oxygen, the basic lead nitrate, for example, and the oxychloride being expressed as follows :—

$$\begin{array}{lcl} O.NO_2 & \qquad & Cl \\ | & & | \\ Pb & & Pb \\ | & & | \\ O & & O \\ | & & | \\ Pb & & Pb \\ | & & | \\ O & & O \\ | & & | \\ Pb & & Pb \\ | & & | \\ O.NO_2 & & Cl. \end{array}$$

The terms basic and acid are sometimes applied to salts with reference to their action on vegetable colours. The normal salts formed by the union of the stronger acids with the alkalis and alkaline earths, such as potassium sulphate, K_2SO_4, barium nitrate, $Ba(NO_3)_2$, &c., are perfectly neutral to vegetable colours, but most other normal salts exhibit either an acid or an alkaline reaction ; thus ferrous sulphate, cupric sulphate, mercuric nitrate, and many others, redden litmus, while the normal carbonates and phosphates of the alkali-metals exhibit a decided alkaline reaction. It is clear, then, that the action of a salt on vegetable colours bears no definite relation to its composition : hence the term *normal*, as applied to salts in which the basic hydrogen of the acid is wholly replaced, is preferable to *neutral*, and the terms *basic* and *acid*, as applied to salts, are best used in the manner above explained with reference to their composition.

When a normal salt containing a monoxide passes by oxidation to a salt containing a sesquioxide, dioxide, or trioxide, the quantity of

acid oxide present is no longer sufficient to saturate the basic oxide. Thus when a solution of ferrous sulphate, $FeSO_4$, or FeO,SO_3 (common green vitriol), is exposed to the air, it absorbs oxygen, and an insoluble ferric salt is produced containing an excess of base, while normal ferric sulphate remains in solution :

$$\underset{\text{Ferrous sulphate.}}{4(FeO,SO_3)} + O_2 = \underset{\text{Normal ferric sulphate.}}{Fe_2O_3,3SO_3} + \underset{\text{Basic ferric sulphate.}}{Fe_2O_3,SO_3}.$$

These basic salts are very often insoluble in water.

Salts containing a proportion of acid oxide larger than is sufficient to form a neutral compound are called anhydro-salts (sometimes, though improperly, acid salts); they may evidently be regarded as compounds of a normal salt with excess of acid oxide ; *e.g.*:

Sodium anhydrosulphate * (bisulphate of soda), $Na_2O(SO_3)_2 = Na_2SO_4.SO_3$

Potassium anhydrochromate (bichromate of potash), $K_2O(CrO_3)_2 = K_2CrO_4.CrO_3$.

The following is a list of the most important inorganic acids, arranged according to their basicity :

Monobasic Acids.

Hydrochloric, . .	HCl	Metaboric, ? .	HBO_2
Hydrobromic, . .	HBr	Metantimonic, ? .	$HSbO_3$
Hydriodic, . .	HI	Hypochlorous, .	$HClO$
Hydrofluoric, . .	HF	Chlorous, . .	$HClO_2$
Nitrous, . . .	HNO_2	Chloric, . .	$HClO_3$
Nitric, . . .	HNO_3	Perchloric, . .	$HClO_4$
Hyposulphurous, .	$H(SHO_2)$	Bromic, . .	$HBrO_3$
Hypophosphorous, .	$H(PH_2O_2)$	Iodic, . . .	HIO_3
Metaphosphoric, .	HPO_3 ?	Metaperiodic, .	HIO_4

Bibasic Acids.

Hydric (water), .	H_2O	Selenious, . .	H_2SeO_3
Sulphydric, . .	H_2S	Selenic, . .	H_2SeO_4
Selenhydric, . .	H_2Se	Tellurous, . .	H_2TeO_3
Tellurhydric, . .	H_2Te	Telluric, . .	H_2TeO_4
Sulphurous, . .	H_2SO_3	Manganic, .	H_2MnO_4
Sulphuric, . .	H_2SO_4	Permanganic, .	$H_2Mn_2O_8$
Pyrosulphuric, .	$H_2S_2O_7$	Chromic, . .	H_2CrO_4
Thiosulphuric, .	$H_2S_2O_3$	Stannic, . .	H_2SnO_3
Dithionic, . .	$H_2S_2O_6$	Metasilicic, . .	H_2SiO_3
Trithionic, . .	$H_2S_3O_6$	Carbonic, . .	H_2CO_3
Tetrathionic, . .	$H_2S_4O_6$	Phosphorous, .	$H_2(PHO_3)$
Pentathionic, . .	$H_2S_5O_6$		

Tribasic Acids.

Orthophosphoric, .	H_3PO_4	Arsenic, . .	H_3AsO_4

Quadribasic Acids.

Pyrophosphoric, .	$H_4P_2O_7$	Orthosilicic, . .	H_4SiO_4.

* The so-called "anhydrosulphates" are now regarded as salts of a distinct acid, pyrosulphuric acid, $H_2S_2O_7$ (p. 135).

The general characters of most of the non-metallic acids and their salts have been already considered; but the phosphates, borates, and silicates require further notice.

Phosphates.—There are three modifications of phosphoric acid: one being monobasic, the other tribasic, and the third quadribasic, as indicated in the preceding table.

Hydrogen phosphide, PH_3, burnt in air or oxygen gas, takes up four atoms of oxygen, and forms trihydric phosphate or tribasic phosphoric acid, PH_3O_4. The same acid is produced by the oxidation of hypophosphorous or phosphorous acid, by oxidising phosphorous with nitric acid; by the decomposition of native calcium phosphate (apatite) and other native phosphates; and by the action of boiling water on phosphoric oxide, P_4O_{10}. This acid forms three distinct classes of metallic salts. With sodium, for example, it forms the three salts, NaH_2PO_4, Na_2HPO_4, and Na_3PO_4, the first two of which, still containing replaceable hydrogen, are constitutionally acid salts, while the third is the normal salt.

If now the monosodic phosphate, NaH_2PO_4, be heated to redness, it gives off one molecule of water, and leaves an anhydrous monosodic phosphate, $NaPO_3$, the aqueous solution of which, when treated with lead nitrate, yields a lead-salt of corresponding composition; thus:—

$$2NaPO_3 + Pb(NO_3)_2 = Pb(PO_3)_2 + 2NaNO_3;$$

and this lead-salt, decomposed by sulphydric acid, yields a monohydric acid having the composition HPO_3, possessing properties quite distinct from those of the trihydric acid above mentioned:—

$$Pb(PO_3)_2 + H_2S = 2HPO_3 + PbS.$$

The trihydric acid which is produced by the oxidation of phosphorus, and by the decomposition of the ordinary native phosphates, is called orthophosphoric acid or ordinary phosphoric acid; the monohydric acid is called metaphosphoric acid.

Metaphosphoric acid and its salts, as usually represented, differ from orthophosphoric acid and the orthophosphates by the want of one or two molecules of water or basic oxide; thus:—

Metaphosphates.		Orthophosphates.		
HPO_3	=	H_3PO_4	−	H_2O
$NaPO_3$	=	NaH_2PO_4	−	H_2O
$Ba(PO_3)_2$	=	$BaH_4(PO_4)_2$	−	$2H_2O$
$AgPO_3$	=	Ag_3PO_4	−	Ag_2O
$Pb(PO_3)_2$	=	$Pb_3(PO_4)_2$	−	$2PbO$.

Accordingly, we find that metaphosphates and orthophosphates are convertible one into the other by the loss or gain of one or two molecules of water or basic oxide.

The metaphosphates are susceptible of five polymeric modifications.

a. *Monometaphosphates*, MPO_3 [M denoting a univalent metal].—

These salts are produced by adding phosphoric acid in excess to solutions of sulphates or nitrates, and heating the evaporated residues to 316° or upwards. The potassium salt is also formed by igniting potassium hydroxide with phosphoric acid in molecular proportion; the ammonium salt by heating ammonium dimetaphosphate to 250°. These metaphosphates are crystalline anhydrous powders, insoluble in water. There are no double salts of this modification.

β. *Dimetaphosphates*, $M_2(PO_3)_2$ and $M''(PO_3)_2$, are formed when aqueous phosphoric acid is heated to 350° with oxide of zinc, manganese, or copper; and the copper salt decomposed by sulphide of potassium or sodium yields potassium or sodium dimetaphosphate. These alkali-metal dimetaphosphates are soluble in water and crystallisable; the rest are insoluble or only slightly soluble.

γ. *Trimetaphosphates*, $M_3(PO_3)_3$.—The sodium salt of this modification is obtained, together with the monometaphosphate, by gently heating microcosmic salt $(NH_4)HNaPO_4$, till the fused mass becomes crystalline; and from this salt other trimetaphosphates may be formed by double decomposition. They are all soluble in water including the silver salt, which may be obtained by slow deposition in large, transparent, monoclinic crystals.

δ. *Tetrametaphosphates*, $M_4(PO_3)_4$.—The lead salt, $Pb_2(PO_3)_4$, is formed by heating lead oxide at 300° with excess of phosphoric acid; and this salt decomposed by sodium sulphide yields the sodium salt, which is viscid and uncrystallisable. By fusing it with copper dimetaphosphate, and leaving the mass to cool gradually, a double salt is obtained having the composition $CuNa_2(PO_3)_4$.

ε. *Hexametaphosphates*, $M_6(PO_3)_6$, discovered by Graham, and obtained by dehydration of dihydric orthophosphates.

The chemical history of these modifications of metaphosphoric acid is, however, still very obscure, and requires further investigation.

Pyrophosphates.—Intermediate between orthophosphates and metaphosphates, there are at least three distinct classes of salts, the most important of which are the pyrophosphates which may be derived from the tetrahydric or quadribasic acid, $H_4P_2O_7$, the normal sodium salt, for example, being $Na_4P_2O_7$, the normal lead salt, $Pb_2P_2O_7$, etc. These salts may be viewed as compounds of orthophosphate and metaphosphate, *e.g.*:

$$Na_4P_2O_7 = Na_3PO_4 + NaPO_3.$$

Sodium pyrophosphate is produced by heating disodium orthophosphate to redness, a molecule of water being then given off:

$$2Na_2HPO_4 = H_2O + Na_4P_2O_7.$$

The aqueous solution of this salt yields insoluble pyrophosphates with lead and silver salts; thus with lead nitrate:

$$Na_4P_2O_7 + 2Pb(NO_3)_2 = 4NaNO + Pb_2P_2O_7;$$

and lead pyrophosphate decomposed by hydrogen sulphide yields hydrogen pyrophosphate or pyrophosphoric acid :

$$Pb_2P_2O_7 + 2H_2S = 2PbS + H_4P_2O_7.$$

Pyrophosphates are easily converted into metaphosphates and orthophosphates, and *vice versa*, by addition or abstraction of water or a metallic base.

Fleitmann and Henneberg, by fusing together a molecule of sodium pyrophosphate, $Na_4P_2O_7$ or Na_3PO_4, $NaPO_3$, with two molecules of metaphosphate $NaPO_3$, obtained a salt having the composition $Na_6P_4O_{13}$ or $Na_3PO_4,3NaPO_3$, which is soluble without decomposition in a small quantity of hot water, and crystallises from its solution by evaporation over oil of vitriol. An excess of hot water decomposes it, but its cold aqueous solution is moderately permanent. Insoluble phosphates of similar composition may be obtained from the sodium salt by double decomposition. Fleitmann and Henneberg obtained another crystallisable but very insoluble salt, having the composition $Na_3PO_4,9NaPO_3$, by fusing together one molecule of sodium pyrophosphate with eight molecules of the metaphosphate ; and insoluble phosphates of similar constitution were obtained from it by double decomposition.

The comparative composition of these different phosphates may be shown by representing them as compounds of phosphoric oxide with metallic oxide, and assigning to them all the quantity of basic oxide contained in the most complex member of the series ; thus—

Orthophosphate, ...	$6Na_2O,2P_2O_5$	$= 4Na_3PO_4$
Pyrophosphate , ...	$6Na_2O,3P_2O_5$	$= 3Na_4P_2O_7$
Fleitmann and Henneberg's phosphate (*a*), .	$6Na_2O,4P_2O_5$	$= 2Na_6P_4O_{13}$
,, ,, ,, (*b*), .	$6Na_2O,5P_2O_5$	$= Na_{12}P_{10}O_{31}$
Metaphosphate, ...	$6Na_2O,6P_2O_5$	$= 12NaPO_3$.

Borates.—There are three series of these salts, analogous to the three principal modifications of the phosphates, and derived respectively from ortho-, meta-, and pyroboric acid (p. 223) ; thus [M denoting a univalent metal] :—

$$\text{Orthoborates, } M_3BO_3 = B(OM)_3$$
$$\text{Metaborates, } MBO_2 = BO(OM)$$
$$\text{Pyroborates, } M_2B_4O_7 = B_4O_5(OM)_2 .$$

The metallic orthoborates are very unstable, the only well-defined orthoborate being the magnesium salt ; but several volatile ethers of similar constitution are known, *e.g.*, triethylic borate, $B(OC_2H_5)_3$. —The *metaborates* are much more stable, *e.g.*, $NaBO_2$ and $Mg(BO_2)_2$. —The *pyroborates* are also stable salts, including sodium pyroborate or borax, $Na_2B_4O_7$, the calcium salt or borocalcite, CaB_4O_7, and boronatrocalcite, $Na_2B_4O_7,2CaB_4O_7$.

Borates of more complex constitution are also known, amongst which are the following minerals :—Larderellite, $(NH_4)_2B_8O_{13}$ Lagonite, $Fe_2B_6O_{12}$, and Boracite, $2Mg_3B_8O_{15}MgCl_2$.

Silicates.—These salts occur very abundantly as natural minerals, and exhibit great diversity of composition; but the most important of them may be arranged in the following groups.

	Oxygen-ratio, $M_2O:SiO_2$.	Formula.	Examples.
Hemisilicates or Orthosilicates.	1 : 1	$2M_2O,SiO_2 = M_4SiO_4$	Olivine $\left.\begin{matrix}Mg''\\Fe''\end{matrix}\right\}SiO_4$.
Monosilicates or Metasilicates.	1 : 2	$M_2O,SiO_2 = M_2SiO_3$	Diopside $(Ca,Mg)''SiO_3$.
Sesquisilicates.	1 : 3	$2M_2O,3SiO_2 = M_4Si_3O_8$	Orthoclase $(KAl''')Si_3O_8$. Stilbite $(Ca''Al'''_2)Si_6O_{16} + 5H_2O$.
Di- or Bi-silicates.	1 : 4	$M_2O,2SiO_2 = M_2Si_2O_5$	Okenite, $Ca''Si_2O_5 + 2H_2O$.

Silicates are sometimes also distinguished by names expressing directly the oxygen-ratio in the silica and metallic oxide, the ratio 1 : 1 giving *Singulosilicates*; 1 : 2, *Disilicates*; 1 : 3, *Trisilicates*; 1 : 4, *Quadrisilicates*, etc.

All silicates are insoluble in water, except those of the alkali-metals, which dissolve with greater facility in proportion as they contain a larger quanity of basic oxide. These salts, known as *soluble glass* or *water-glass*, are used for making artificial stone, and preserving natural stone from decay; also for rendering muslin and other light fabrics uninflammable; and for a peculiar style of mural painting.

Some silicates are entirely decomposed by heating them in the state of powder, with hydrochloric or nitric acid, the bases being dissolved and silica separated. Others, on the contrary, resist the action of all acids except hydrofluoric; but all without exception become soluble in dilute nitric or hydrochloric acid, after fusion with from 3 to 5 times their weight of hydroxide or carbonate of potassium or sodium, or with carbonate of barium, or calcium, or with lead oxide, the mineral being completely disintegrated, and the solution yielding on evaporation, first a jelly and then a dry residue, of which the part insoluble in hot hydrochloric acid exhibits the characters of silica.—Silicates heated in a platinum vessel with hydrofluoric acid, or with fluorspar and strong sulphuric acid, give off gaseous fluoride of silicon.

Metallic Sulphides.—These compounds correspond, for the most part, in composition with the oxides: thus there are two sulphides of antimony, Sb_2S_3 (or Sb_4O_6), and Sb_2S_5, corresponding with the oxides, Sb_4O_6 and Sb_2O_5; also two sulphides of mercury, Hg_2S and HgS, analogous to the oxides, Hg_2O and HgO. Occasionally, however, we meet with oxides to which there are no corresponding sulphides (manganese dioxide, for example), and more

frequently with sulphides to which there are no corresponding oxides, the most remarkable of which are perhaps the alkaline polysulphides. Potassium, for example, forms the series of sulphides, K_2S, K_2S_2, K_2S_3, K_2S_4, and K_2S_5, the third and fifth of which have no analogues in the oxygen series.

There are also hydrosulphides analogous to the hydroxides, and containing the elements of a metallic sulphide and hydrogen sulphide, or sulphydric acid: *e.g.*, potassium hydrosulphide, $K_2S,H_2S = 2KHS$; lead hydrosulphide, $PbS,H_2S = PbH_2S_2$. Hydrosulphides and sulphides may be derived from sulphydric acid by partial or total replacement of the hydrogen by metals, just as metallic hydroxides and oxides are derived from water.

Many metallic sulphides occur as natural minerals, especially the sulphides of zinc, lead, copper, and mercury, which afford valuable ores for the extraction of the metals, and iron bisulphide or iron pyrites, FeS_2, which is largely used as a source of sulphur, and for the preparation of ferrous sulphate.

Sulphides are formed artificially by heating metals with sulphur; by the action of metals on gaseous hydrogen sulphide; by the reduction of sulphates with hydrogen or charcoal; by heating metallic oxides in contact with gaseous hydrogen sulphide or vapour of carbon bisulphide; and by precipitation of metallic solutions with hydrogen sulphide or a sulphide of alkali-metal. Some metals, as copper, lead, silver, bismuth, mercury, and cadmium, are precipitated from their acid solutions by hydrogen sulphide, passed into them as gas, or added in aqueous solution, the sulphides of these metals being insoluble in dilute acids; others, as iron, cobalt, nickel, manganese, zinc, and uranium, form sulphides which are soluble in acids, and these are precipitated by hydrogen sulphide only from alkaline solutions, or by ammonium or potassium sulphide from neutral solutions. Many of these sulphides exhibit characteristic colours, which serve as indications of the presence of the respective metals in solution.

Metallic sulphides are also formed by the reduction of sulphates with organic substances; many native sulphides have doubtless been formed in this way.

The physical characters of some metallic sulphides closely resemble those of the metals in certain particulars, such as the peculiar opacity, lustre, and density, especially when they are crystallised. They are generally crystallisable, brittle, and of a grey, pale yellow, or dark brown colour. The sulphides of the alkali-metals are soluble in water; most of the others are insoluble. They are more frequently fusible than the corresponding oxides, and some are volatilisable, as mercury sulphide and arsenic sulphide.

Many sulphides, when heated out of contact with atmospheric air, do not undergo any decomposition; this is the case chiefly with those containing the smallest proportions of sulphur, such as the monosulphides of iron and zinc. Sulphides containing larger proportions of sulphur are partially decomposed by heat, losing part of

their sulphur, and being converted into lower sulphides ; as in the case of iron bisulphide. The sulphides of gold and platinum are completely reduced by heat.

Some sulphides may be decomposed by the simultaneous action of heat and of substances capable of combining with sulphur. Thus, for instance, silver, copper, bismuth, tin, and antimony sulphides are reduced by hydrogen ; copper, lead, mercury, and antimony sulphides are reduced by heating with iron.

Sulphides which are not reduced by heat alone are always decomposed when heated in contact with oxygen or atmospheric air. Those of the alkali-metals and earth-metals are converted into sulphates by this means. Zinc, iron, manganese, copper, lead, and bismuth sulphides are converted into oxides, and sulphurous oxide is produced ; but when the temperature is not above dull redness, a certain quantity of sulphate is also formed by direct oxidation. Mercury and silver sulphides are completely reduced to the metallic state. Some native sulphides gradually undergo alteration by mere exposure to the air ; but the action is then generally limited to the production of sulphates, unless the oxidation takes place so rapidly that the heat generated is sufficient to decompose the sulphate first produced. In the production of some metals for use in the arts, the separation of sulphur from the native minerals is effected chiefly by means of this action in the operation of roasting.

Metallic sulphides are decomposed in like manner when heated with metallic oxides in suitable proportions, yielding sulphurous oxide and the metal of both the sulphide and oxide. Lead is reduced from the native sulphide in this manner.

Many metallic sulphides are decomposed by acids in presence of water, sulphuretted hydrogen being evolved while the metal enters into combination with the negative radicle of the acid. Nitric acid when concentrated decomposes most sulphides, with formation of metallic oxide, sulphuric acid, sulphur, and a lower oxide of nitrogen. Nitromuriatic acid acts in a similar manner, but still more energetically.

Sulphur-Salts.—The sulphides of the more electro-positive metals unite with those of the more negative metals, and of the non-metallic elements, forming sulphur-salts, analogous in composition to the oxygen salts, *e.g.* :

Carbonate, $K_2CO_3 = K_2O.CO_2$
Thiocarbonate, $K_2CS_3 = K_2S.CS_2$

Arseniate, $K_3AsO_4 = \frac{1}{2}(3K_2O.AsO_{25})$
Thioarseniate, $K_3AsS_4 = \frac{1}{2}(3K_2S.AsS_{25})$.

Antimoniate, $2K_3SbO_4 = 3K_2O,Sb_2O_5$
Thioantimoniate, $2K_3SbS_4 = 3K_2S,Sb_2S_5$.

Selenides.—These compounds are analogous in composition and in many of their properties, to the sulphides, and unite one with the other, forming selenio-salts analogous to the oxygen and sulphur salts.

Tellurides are analogous in composition and properties to the

sulphides and selenides, but they likewise exhibit some of the characters of metallic alloys.

Carbides.—These compounds are formed by direct union of metals with carbon or by heating their oxides with excess of carbon to the high temperature of the electric arc. Gold, bismuth, lead, and tin do not combine with carbon, and fused copper takes up only a minute quantity. Silver at its boiling point combines with a little carbon, which is, however, deposited on cooling in the form of graphite. Iron also dissolves carbon, some of which separates on cooling in the form of graphite or when under great pressure in the form of diamond : a portion of the carbon remains combined in the form of a white hard crystalline alloy (see *Cast Iron*). Most of the other elements yield definite crystalline carbides which, by contact with water, are decomposed, yielding an oxide of the metal and a hydrocarbon. Calcium carbide is now manufactured on a somewhat large scale for the production of acetylene.

Metals also form definite compounds with nitrogen, phosphorus, silicon, and boron, but these compounds are comparatively unimportant.

Fusibility of Metallic Salts.

Experiment.—The following is a convenient method for determining the melting points of bodies which fuse at moderate temperatures. A glass tube is drawn out until its sides become very thin and its bore nearly capillary, and a small quantity of the substance under investigation is introduced. The tube is then sealed at the bottom and placed in a glass vessel containing water (or paraffin or sulphuric acid if the substance melts above 100°), and standing on a small sand-bath by which the temperature can be slowly raised. The liquid is heated till the substance melts, then allowed to cool slowly to the solidifying point, and again warmed, these observations being repeated, and the temperatures of liquefaction and solidification being each time noted, until several nearly concordant results have been obtained. The mean of all these is taken as the true melting point of the substance.

For determining the melting points of bodies which melt at higher temperatures, such as metallic salts, a method has been given by Carnelley, depending on the following principle : When a small quantity of a salt is placed in a weighed platinum crucible suspended in the flame of a Bunsen burner or a blow-pipe, and the crucible, at the instant when the salt fuses, is dropped into a known weight of water of known temperature, the rise in temperature of the water being then noted, the temperature at which the fusion occurred may be found from the equation—

$$T = \theta + \frac{(W + w)\, r\, (\theta - t)}{Ms},$$

in which W denotes the weight of water in the calorimeter ; w the thermal value of the calorimeter + mercury and glass of thermometer in grams of water ; M the weight of the crucible ; r the specific heat

of water ; s the specific heat of platinum (from 0° to T) ; t the initial, and θ the final temperature of the water.

The following table exhibits the melting points of all important metallic salts of inorganic acids, which have been carefully determined. The former portion of the list includes those which have been directly observed by the thermometer, the latter those which have been estimated by the calorimetric method.

Observed by the Thermometer.

Name of Salt.	Formula.	Melting Point. Centigrade.
Arsenic tri-iodide, . . .	AsI_3	146
Boric acid, ...	H_3BO_3	184
Silver nitrate, ...	$AgNO_3$	218
Mercuric bromide, . . .	$HgBr_2$	244
Lithium nitrate, ...	$LiNO_3$	264
Thallium carbonate, . . .	Tl_2CO_3	272
Mercuric chloride, . . .	$HgCl_2$	288
Sodium chlorate, ...	$NaClO_3$	302
Sodium nitrate, ...	$NaNO_3$	319
Potassium nitrate, . . .	KNO_3	339
Potassium chlorate, . . .	$KClO_3$	359

Estimated by the Calorimetric Method.

Name of Salt.	Formula.	Melting Point. Centigrade.
Lead iodide, ...	PbI_2	383
Zinc bromide, ...	$ZnBr_2$	394
Cadmium iodide, ...	CdI_2	404
Barium chlorate, ...	$Ba(ClO_3)_2$	414
Silver bromide, ...	$AgBr$	427
Thallium chloride, . . .	$TlCl$	427
Cuprous chloride, ...	Cu_2Cl_2	434
Thallium iodide, ...	TlI	439
Lithium iodide, ...	LiI	446
Zinc iodide, ...	ZnI_2	446
Silver chloride, ...	$AgCl$	451
Thallium bromide, . . .	$TlBr$	458
Silver metaphosphate, . . .	$AgPO_3$	482
Cupric chloride, ...	$CuCl_2$	498
Lead chloride, ...	$PbCl_2$	498
Lead bromide, ...	$PbBr_2$	499
Strontium iodide, ...	SrI_2	507
Cadmium fluoride, . . .	CdF_2	520
Silver iodide, ...	AgI	527
Cadmium chloride, . . .	$CdCl_2$	541
Lithium bromide, ...	$LiBr$	547
Calcium nitrate, ...	$Ca(NO_3)_2$	561
Borax (anhydrous), . . .	$Na_2B_4O_7$	561

Estimated by the Calorimetric Method—continued.

Sodium metavanadate, . . .	$NaVO_3$	562
Thallium vanadate, . . .	Tl_3VO_4	566
Cadmium bromide, . . .	$CdBr_2$	571
Barium nitrate, ...	$Ba(NO_3)_2$	593
Silver pyrophosphate, . . .	$Ag_4P_2O_7$	585
Lithium chloride, . . .	$LiCl$	598
Cuprous iodide, ...	Cu_2I_2	601
Sodium metaphosphate, . .	$NaPO_3$	617
Sodium iodide, ...	NaI	628
Strontium bromide, . . .	$SrBr_2$	630
Cadmium iodide, ...	CdI_2	631
Thallium sulphate, . . .	Tl_2SO_4	632
Potassium iodide, ...	KI	634
Rubidium iodide, ...	RbI	642
Strontium nitrate, . . .	$Sr(NO_3)$	645
Sodium pyrovanadate, . . .	$Na_4V_2O_7$	654
Silver sulphate, ...	Ag_2SO_4	654
Calcium bromide, . . .	$CaBr_2$	676
Rubidium bromide, . . .	$RbBr$	683
Lithium carbonate, . . .	Li_2CO_3	695
Magnesium bromide, . . .	$MgBr_2$	695
Potassium bromide, . . .	KBr	699
Sodium bromide, ...	$NaBr$	708
Magnesium chloride, . . .	$MgCl_2$	708
Rubidium chloride, . . .	$RbCl$	710
Calcium chloride, . . .	$CaCl_2$	719
Potassium chloride, . . .	KCl	734
Sodium chloride, ...	$NaCl$	772
Potassium fluoride, . . .	KF	789
Barium bromide, ...	$BaBr_2$	812
Sodium carbonate, . . .	Na_2CO_3	814
Lithium sulphate, . . .	Li_2SO_4	818
Strontium chloride, . . .	$SrCl_2$	825
Potassium carbonate, . . .	K_2CO_3	834
Sodium sulphate, ...	Na_2SO_4	861
Calcium fluoride, ...	CaF_2	above 902

Salts containing water of crystallisation usually melt at a relatively low temperature. The following are a few examples :—

Name.	Formula.	Melting Point.
Sodium chromate, . . .	$Na_2CrO_4 10H_2O$	23
Calcium chloride, . . .	$CaCl_2 6H_2O$	28
Sodium sulphate, . . .	$Na_2SO_4 10H_2O$	34
Sodium carbonate, . .	$Na_2CO_3 10H_2O$	34
Sodium phosphate, . .	$Na_2HPO_4 12H_2O$	35
Sodium thiosulphate, . .	$Na_2S_2O_3 5H_2O$	48·5
Alum, ...	$KAl(SO_4)_2 12H_2O$	84·5
Strontium chloride, . .	$SrCl_2 6H_2O$	112
Copper nitrate, . . .	$Cu(NO_3)_2 3H_2O$	114·5

Solubility of Salts in Water.

The combination of salts with water and their solubility have already been referred to (p. 79).

Why some salts dissolve in water and others do not is a question which at present cannot be answered, but a few general statements may serve as useful memoranda.

Nearly all salts which unite with water of crystallisation are easily soluble in water, the only prominent exception being calcium sulphate, $CaSO_4 2H_2O$, which is only slightly soluble.

Normal nitrates are all soluble in water, with the exception of a few which are decomposed by water, *e.g.*, $Bi(NO_3)_3$.

Chlorides are generally soluble, the chief exceptions being silver chloride and mercurous chloride, which are insoluble; lead chloride, which dissolves to a slight extent only; and chlorides, such as antimonious chloride, which are decomposed by water.

Sulphates, with the exception of lead, barium, and strontium sulphates, are soluble. Mercuric and antimonic sulphates are decomposed, forming insoluble oxysalts.

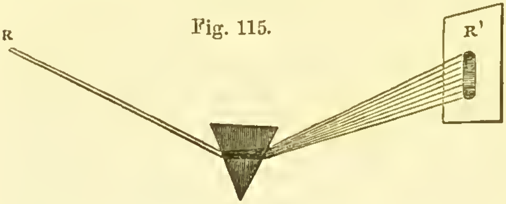
Sulphides, carbonates, and phosphates of all except the alkali-metals, are usually insoluble in water.

The solubility of a salt usually increases with rise of temperature, and this is doubtless connected with the fact that in a series of salts of similar constitution the solubility is directly related to the fusibility. Comparing calcium and strontium chlorides, for example, the calcium compound, whether hydrated or anhydrous, has the lower melting point; it is also by far the more soluble at all observed temperatures.

THE SPECTROSCOPE AND SPECTRAL ANALYSIS.

The light of the sun and of celestial bodies in general, as well as that of the electric spark and of all ordinary flames, is of a compound nature. If a ray of light from any of the sources mentioned be admitted into a dark room by a small hole in a shutter, or otherwise, and suffered to fall upon a glass prism, in the manner shown in fig. 115, it will not only be refracted from its straight course, but will be decomposed into a number of coloured rays, which may be received upon a white screen placed behind the prism. When solar light is employed, the colours are extremely brilliant, and spread into an oblong space of considerable length.

Fig. 115.



The prism being placed with its base upwards, as in the figure, the upper part of this image, or *spectrum*, will be violet and the lower red, the intermediate portion, commencing from the violet, being indigo, blue, green, yellow, and orange, all graduating imperceptibly into each other. This is the celebrated experiment of Sir Isaac Newton; from it he drew the inference that white light is composed of seven primitive colours, the rays of which are differently refrangible by the same medium, and hence capable of being thus separated. The violet rays are most refrangible, and the red rays least.

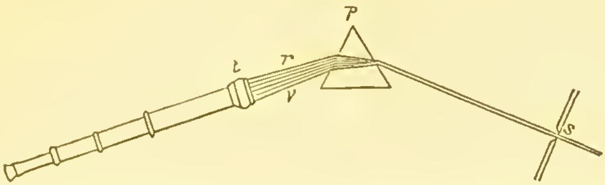
Bodies of the same mean refractive power do not always equally disperse or spread out the differently coloured rays to the same extent; because the principal yellow or red rays, for instance, are equally refracted by two prisms of different materials, it does not follow that the blue or the violet will be similarly affected. Hence, prisms of different varieties of glass, or other transparent substances, give, under similar circumstances, very different spectra, both as respects the length of the image, and the relative extent of the coloured bands.

The appearance of the spectrum may also vary with the nature of the source of light: the investigation of these differences, however, involves the use of a more delicate apparatus. Fig. 116 shows the principle of such an apparatus, which is called a *spectroscope*. The light, passing through a fine slit, *s*, impinges upon a flint-glass prism, *p*, by which it is dispersed. The decomposed light emerges from the prism in several directions between *r* (red rays) and *v* (violet rays); and the spectrum thus produced is observed by the telescope,

t, which receives only part of it at once; but the several parts may be readily examined by turning slightly either the prism or the telescope.

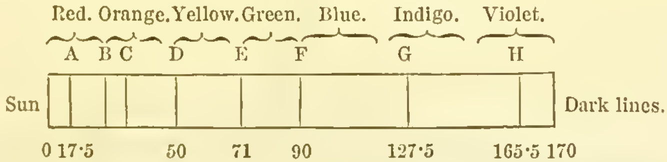
If the solar spectrum be examined in this manner, numerous dark lines parallel with the edge of the prism are observed. They were discovered in 1802 by Wollaston, and subsequently more minutely

Fig. 116.



investigated by Fraunhofer. They are generally known as Fraunhofer's lines. These dark lines, which exist in great numbers, and of very varying strength, are irregularly distributed over the whole spectrum. Some of them, in consequence of their peculiar strength and their relative positions, may always be easily recognised. Fig. 117 shows the relative positions of the more conspicuous lines on a scale divided into 170 equal parts (*see* also the frontispiece to this volume). The same dark lines, though paler, and much more difficult to recognise, are observed in the spectrum of planets lighted by

Fig. 117.



the sun; for instance, in the light emanating from Venus. On the other hand, the dark lines observed in the spectra which are produced by the light emanating from fixed stars—from Sirius, for instance—differ in position from those previously mentioned.

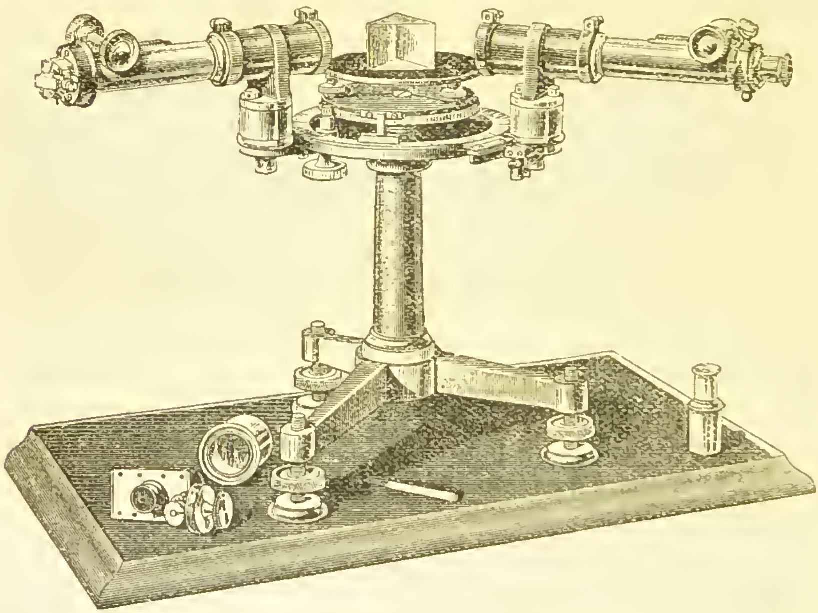
Sources of light which contain no volatile constituents—incandescent platinum wire, for example—furnish continuous spectra, exhibiting no such lines. But if volatile substances be present in the source of light, bright lines are observed in the spectrum, which are frequently characteristic of the volatile substances.

The spectra which are produced by the light developed by the electric discharge in very rarefied gases, consist of bright lines and dark spaces between the lines, varying considerably with different gases. When an electric discharge occurs in a mixture of two gases, the spectrum thus obtained exhibits simultaneously the peculiar spectra belonging to the two gases of which the mixture consists. When the experiment is made in gaseous compounds capable of being decomposed by the electric discharge, this decomposition is

indicated by the spectra of the separated constituents becoming perceptible.

Many years ago the spectra of coloured flames were examined by Sir John Herschel, Fox Talbot, and W. A. Miller. The modern form of spectroscope, however, was introduced by Kirchhoff and Bunsen, who investigated the spectra furnished by the incandescence of volatile substances ; these researches have enriched chemistry with the method of analysis by spectrum observations. In order to recognise one of the metals of the alkalis or of the alkaline earths, it is generally sufficient to introduce a minute quantity of a moderately volatile compound of the metal, on the loop of a platinum wire, into the edge of the very hot, but scarcely luminous Bunsen flame, and to examine the spectrum which is furnished by the flame containing the vapour of the metal or its

Fig. 118.



compound. Fig. 118 exhibits the apparatus which is used in performing experiments of this description. The light of the flame in which the metallic compound is evaporated passes through the fine slit in the disc, into a tube the opposite end of which is provided with a convex lens. This lens collects the rays diverging from the slit, and throws them parallel upon the prism. The light is decomposed by the prism, and the spectrum thus obtained is observed by means of the telescope, which may be turned round the axis of the stand carrying the prism. Foreign light is excluded by a dark cloth thrown over the prism. Arrangements can also be

made for sending the light from different sources through the same prism at different heights, whereby their spectra, the solar spectrum, for instance, and that of a flame, may be placed in a parallel position, the one above the other, and thus be compared.

The spectra of flames in which different substances are volatilised frequently exhibit such characteristically distinct phenomena, that they may be used with the greatest advantage for the discrimination of these substances. Thus the spectrum of a flame containing sodium exhibits a bright line in the yellow portion, the spectrum of potassium a characteristic bright line at the extreme limit of the red, and another at the opposite violet limit of the spectrum. Lithium shows a brilliant line in the red, and a paler line in the yellow portion; strontium a bright line in the blue, one in the orange, and six less distinct ones in the red portion of the spectrum. The *frontispiece* exhibits the most remarkable of the dark lines of the solar spectrum (Fraunhofer's lines), and the position of the bright lines in the spectra of flames containing the vapours of compounds of the metals of the alkalis and alkaline earths, also of the metals thallium and indium.

The delicacy of these spectral reactions is very considerable, but unequal in the case of different metals. The presence of $\frac{1}{200,000,000}$ grain of sodium in the flame is still easily recognisable by the bright yellow line in the spectrum. Lithium, when introduced in the form of a volatile compound, imparts to the flame a red colour; but this coloration is no longer perceptible when a volatile sodium compound is simultaneously present, the yellow coloration of the flame predominating under such circumstances. But when a mixture of one part of lithium and 1000 parts of sodium is volatilised in a flame, the spectrum of the flame exhibits, together with the bright yellow sodium line, the red line characteristic of lithium. The observation of bright lines not belonging to any of the previously known bodies has led to the discovery of new elements. Thus, Bunsen and Kirchhoff, when examining the spectrum of the flame in which a mixture of alkaline salts was evaporated, observed some bright lines, which could not be attributed to any of the known elements, and were thus led to the discovery of the two metals, cæsium and rubidium. By the same method, a new element, thallium, was discovered in 1861 by Crookes; another, called indium, in 1863, by Reich and Richter; a third, called gallium, in 1875, by Lecoq de Boisbaudran; several of the earth-metals, by Cleve, Delafontaine, Marignac, and Nilson; and in 1895 the strange new gas, helium, was recognised by Ramsay.

For the examination of the bright lines in the spectra of metals, the electric spark may be conveniently employed as a source of light. Small quantities of the metal are invariably volatilised; and the spectrum developed by the electric light exhibits the bright lines characteristic of the metal employed. These lines were observed by Wheatstone as early as 1835. This method of investigation is more

especially applicable to the examination of the spectra of the heavy metals. The spark passes between two points of the metal or between a platinum wire and a solution of a compound of the metal.

Absorption Spectra.—By a series of theoretical considerations, Kirchhoff arrived at the conclusion that the spectrum of an incandescent gas is reversed—*i.e.*, that the bright lines become dark lines—if there be behind the incandescent gas a very luminous source of light, which by itself furnishes a continuous spectrum. Kirchhoff and Bunsen fully confirmed this conclusion by experiment. Thus a volatile lithium salt produces, as just pointed out, a very distinct bright line in the red portion of the spectrum; but if bright sunlight, or the light emitted by a solid body heated to the most powerful incandescence, be allowed to fall through the flame upon the prisms, the spectrum exhibits, in the place of this bright line, a black line similar in every respect to Fraunhofer's lines in the solar spectrum. In like manner the bright strontium line is reversed into a dark line. All the Fraunhofer lines in the solar spectrum are believed to be bright lines thus reversed. According to this conception, the sun is surrounded by a luminous atmosphere, containing a number of volatilised substances, which would give rise in the spectrum to certain bright lines, if the light of the solar atmosphere alone could reach the prisms; but the intense light of the powerfully incandescent body of the sun which passes through the solar atmosphere, causes these bright lines to be reversed and to appear as dark lines on the ordinary solar spectrum. The chemical constituents of the solar atmosphere have been investigated by ascertaining the elements which, when in the state of incandescent vapour, develop bright spectral lines, coinciding with Fraunhofer's lines in the solar spectrum. Fraunhofer's line D (fig. 117) coincides accurately with the bright spectral line of sodium, and may be artificially produced by reversing the latter; sodium would thus appear to be a constituent of the solar atmosphere. A large number of bright lines perceptible in the spectrum of iron correspond, both as to position and distinction, most exactly with the same number of dark lines in the solar spectrum, and, accordingly, iron, in the state of vapour, is believed to be present in the solar atmosphere.

The relative quantities of the several coloured rays absorbed by a coloured medium of given thickness may be observed by viewing through a prism a line of light which has passed through the coloured medium; the spectrum will then be seen to be diminished in brightness in some parts, and perhaps cut off altogether in others. This mode of observation is often of great use in chemical analysis, as many coloured substances when thus examined afford very characteristic spectra, the peculiarities of which may often be distinguished, even though the solution of the substance under examination contains a sufficient amount of coloured impurities to change its colour very considerably.

To observe the whole progress of the absorption, different degrees

of strength must be used in succession, beginning with a strength which does not render any part of the spectrum absolutely black, unless it be one or more very narrow bands, as otherwise the most distinctive features of the absorption might be missed. If the solution be contained in a wedge-shaped vessel instead of a test-tube, the progress of the absorption may be watched in a continuous manner by sliding the vessel before the eye. Some observers prefer using a wedge-shaped vessel in combination with the slit, the slit being perpendicular to the edge of the wedge. In this case each element of the slit forms an elementary spectrum corresponding with a thickness of the solution which increases in a continuous manner from the edge of the wedge, where it vanishes.

Fig. 119 represents the effect produced in this way by a solution

Fig. 119.

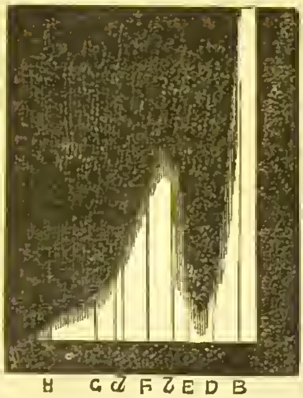
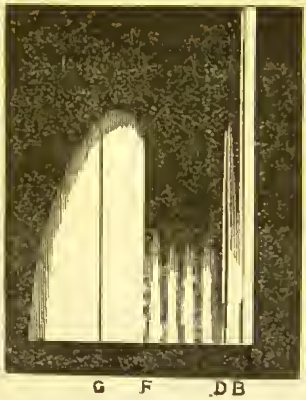


Fig. 120.



of chromic chloride, and fig. 120 that produced by a solution of potassium permanganate.

The right hand side of these figures corresponds with the red end of the spectrum; the letters refer to Fraunhofer's lines. The lower part of each figure shows the pure spectrum seen through the thinnest part of the wedge; and the progress of the absorption, as the thickness of the liquid increases, is seen by the gradual obliteration of the spectrum towards the upper part of the figures.

METALS OF THE ALKALIS.

This group includes five metals, viz., potassium, sodium, rubidium, cæsium, and lithium. They are soft, easily fusible, volatile at higher temperatures; combine very energetically with oxygen; decompose water at all temperatures; and form strongly basic oxides, which are very soluble in water, yielding powerfully caustic and alkaline hydroxides, not decomposable by heat. Their carbonates, sulphates, phosphates, and sulphides are soluble in water. They may be divided into two sub-groups, one of which includes lithium and sodium, distinguished by the tendency many of their salts exhibit to unite with water of crystallisation, and by the ready solubility in water of their acid tartrates and platino-chlorides; the other includes potassium, rubidium and cæsium, which are distinguished from the former by greater chemical activity of the metals and of their hydroxides, also by the insolubility of their platino-chlorides. The relations of the atomic weights are shown below, and it will be seen that they form series comparable with those of the halogens, the sulphur group and others.

Atomic Weights.

$$\left.\begin{array}{ll}\text{Lithium,} \quad . \quad . \quad . \quad . & 7 \\ \text{Sodium,} \quad . \quad . \quad . \quad . & 23 \\ \text{Potassium,} \quad . \quad . \quad . \quad . & 39{\cdot}1\end{array}\right\} \frac{7+39{\cdot}1}{2} = 23{\cdot}0$$

$$\left.\begin{array}{ll}\text{Potassium,} \quad . \quad . \quad . \quad . & 39{\cdot}1 \\ \text{Rubidium,} \quad . \quad . \quad . \quad . & 85{\cdot}5 \\ \text{Cæsium,} \quad . \quad . \quad . \quad . & 133\end{array}\right\} \frac{39{\cdot}1+133}{2} = 86{\cdot}0$$

The hypothetical radicle ammonium is usually added to the list of alkali-metals, on account of the general similarity of its compounds to those of potassium and sodium.

POTASSIUM.

Symbol K (Kalium). Atomic weight, 39.

Potassium was discovered in 1807 by Sir H. Davy, who obtained it in very small quantity by exposing a piece of moistened potassium hydroxide to the action of a powerful voltaic battery, the alkali being placed between a pair of platinum plates connected with the apparatus. Processes have since been devised for obtaining this metal in almost any quantity that can be desired.

An intimate mixture of dry potassium carbonate and charcoal is prepared by calcining, in a covered iron pot, the crude tartar of commerce; when cold it is rubbed to powder, mixed with one-tenth part of charcoal in small lumps, and quickly transferred to an iron retort; the latter may be one of the iron bottles in which mercury is imported. The retort is introduced into a furnace *a* (fig. 121), and placed horizontally on supports of fire-brick, *f f*. A wrought-iron tube *d*, 4 inches long, serves to convey the vapours of potassium into a receiver *e*, formed of two pieces of sheet iron *a b* (fig. 122), which are fitted closely to each other, so as to form a shallow box only a quarter of an inch deep, and are kept together by clamp screws. The receiver is open at both ends, the socket fitting upon the neck of the iron bottle. The object of giving the receiver this flattened form is to insure the rapid cooling of the potassium, and thus to withdraw it from the action of the carbon monoxide, which is disengaged during the entire process, and has a strong tendency to unite with the potassium, forming a dangerously explosive compound. Before connecting the receiver with the tube *d*, the iron bottle is heated to dull redness. The temperature is then raised to a full reddish-white heat, when vapours of potassium begin to appear and burn with a bright flame. The receiver is then adjusted to the end of the tube, which must not project more than a quarter of an inch through the iron plate forming the front wall of the furnace; otherwise the tube is liable to be obstructed by the accumulation of solid potassium, or of the explosive compound above mentioned. Should any obstruction occur, it must be removed by thrusting in an iron bar, and, if this fail, the fire must be immediately withdrawn

Fig. 121.

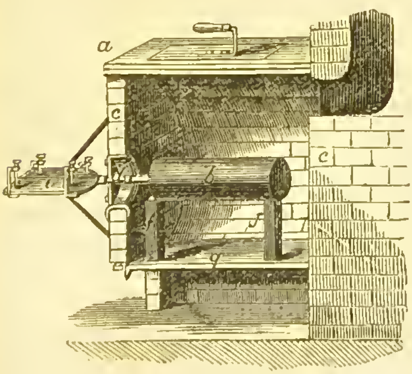
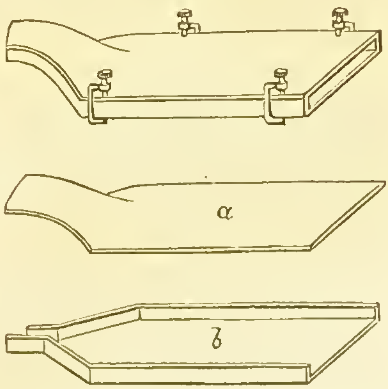


Fig. 122.



The receiver is kept cool by the application of a wet cloth to its outside. When the operation is complete, the receiver with the potassium is removed and immediately plunged into a vessel of rectified petroleum provided with a cover, and kept cool by immersion in water. When the apparatus is sufficiently cooled, the potassium is detached and preserved under petroleum.

The chief reaction which occurs is as follows :

$$K_2CO_3 + 2C = K_2 + 3CO.$$

The yield of metal is, however, much less than the amount calculated from this equation. Potassium is now obtained by the improved process which will be described in connection with sodium in which the alkaline hydroxide is employed as the material and hydrogen, not carbonic oxide, is the gas evolved.

If the potassium be wanted absolutely pure, it must be afterwards re-distilled in an iron retort, into which some petroleum has been put, that its vapour may expel the air, and prevent oxidation of the metal.

Potassium is a brillant white metal, with a high degree of lustre ; at the common temperature of the air it is soft, and may be easily cut with a knife, but at 0° it is brittle and crystalline. It melts completely at 62·5°, and distils at a low red heat. It floats on water, its density being only 0·865.

Exposed to the air, potassium oxidises instantly, a tarnish covering the surface of the metal, which quickly thickens to a crust of caustic potash. Thrown upon water, it takes fire spontaneously, and burns with a beautiful purple flame, yielding an alkaline solution.

Experiment.—Throw into a dish of cold water a small piece of potassium (about one-fourth the size of a pea). Observe that the metal floats upon the surface of the water ; the hydrogen which escapes becomes immediately ignited and burns with a purple flame. The action may be watched closely if the dish be covered with a sheet of glass, otherwise there is danger to the face from the sputtering which occurs at the end of the action. Dip red litmus paper into the solution, and observe that its colour changes to blue, showing the alkalinity of the resulting hydroxide, KHO.

Potassium Chloride, KCl, occurs in sea-water and in many mineral springs, and is the chief constituent of the "potash-salt" of Stassfurt near Magdeburg, which forms a layer 80 to 100 feet thick, lying above the rock-salt, and consists mainly of carnallite, $KCl,MgCl_2+6H_2O$, and kieserite, $MgSO_4+H_2O$, interspersed with veins of sylvine KCl, and several calcium and magnesium salts. All these minerals are very deliquescent, and the entire deposit appears to have been formed by the drying up of an inland sea or salt-water lake. Similar beds occur at Kalusz in Galicia.

The preparation of potassium chloride from the "potash-salt" depends upon the fact that carnallite forms only in solutions containing excess of magnesium chloride, so that when the salt is dissolved in hot water, and the solution is left to cool, no double salt separates, but the more soluble chloride of magnesium remains in solution, while part of the potassium chloride crystallises out. The mother-liquors are then further treated for the recovery of the remaining quantity.

The "potash-salt" is first dissolved in cold water ; the solution is

heated by a steam-pipe conveying steam at 120°, and continually stirred by revolving arms, to facilitate solution; and the liquid, after standing for ten hours, is decanted from the insoluble matter. The clear solution is completely saturated with the chlorides of potassium and magnesium, and contains also small quantities of sodium chloride and magnesium sulphate. It is transferred to a series of crystallising vessels in which crystals are deposited containing from 60 to 70 per cent. of potassium chloride, a charge of 20,000 kilograms of "potash-salt" yielding from 16,000 to 17,000 kilograms of this impure chloride of potassium. The crystals are washed with water to remove the adhering mother-liquor and the magnesium chloride, after which they contain 80 per cent. of potassium chloride.

Potassium chloride is obtained in like manner from the mother-liquor of sea water and from certain mineral springs. In the *salines* on the west and south coasts of France, the mother-liquors remaining after the common salt has been deposited are preserved in reservoirs during the summer, when a mixture of magnesium sulphate and common salt separates out. The mother-liquor from this is evaporated in shallow pans, and thus converted into carnallite, which is worked up as above described.

Potassium chloride closely resembles common salt in appearance, and crystallises like the latter, in cubes. The crystals dissolve in three parts of cold, and in a much smaller quantity of boiling water; they are anhydrous, have a simple saline taste, with slight bitterness and fuse at a red heat. Potassium chloride is volatilised by a very high temperature.

Potassium chloride is used for the preparation of other potassium salts, as the nitrate, chlorate, carbonate, and chromate, and of potash-alum. The impure salt is employed in the composition of artificial manures.

Potassium Iodide, KI.—When iodine is added to a strong solution of caustic potash free from carbonate, it is dissolved in large quantity, forming a colourless solution containing potassium iodide and iodate:

$$6KHO + 3I_2 = 5KI + KIO_3 + 3H_2O.$$

The reaction is the same as in the analogous case with chlorine. When the solution begins to be permanently coloured by the iodine, it is evaporated to dryness, and the residue heated to redness, by which the iodate is entirely converted into iodide. The mass is then dissolved in water, and, after filtration, made to crystallise.

Experiment.—Pour into an evaporating dish half a pint of ordinary 5 per cent. solution of potash, place the dish over a rose-burner and heat it; add iodine in small doses till the liquid acquires a permanent yellow colour, then boil the whole rapidly to dryness. Grind the dry salts in a mortar with a little charcoal, put the mixture into a crucible, and heat to low redness. Let the mass cool, dissolve it in

water, filter the solution, and evaporate it to a small bulk. Then leave it to crystallise.

Potassium iodide crystallises in cubes, which are often, from some unexplained cause, milk-white and opaque. It is anhydrous, melts readily when heated, at 639° according to Carnelley, and volatilises at higher temperatures. The salt is very soluble in water, but when pure does not deliquesce in a moderately dry atmosphere: it is dissolved by alcohol.

Solution of potassium iodide, like the solutions of all the soluble iodides, dissolves a large quantity of free iodine, forming a deep-brown liquid, not decomposed by water.

Potassium Bromide, KBr, may be obtained by processes exactly similar to those just described, substituting bromine for the iodine. It is a colourless and very soluble salt, quite indistinguishable in appearance and general characters from the iodide.

Potassium Oxides.—Potassium forms three oxides, K_2O, K_2O_2, and K_2O_4, also a hydroxide, KHO, corresponding with the monoxide.

The *monoxide*, K_2O, also called *anhydrous potash*, or *potassa*, is formed when potassium in thin slices is exposed at ordinary temperatures to dry air free from carbon dioxide.

It is white, very deliquescent and caustic, combines energetically with water, forming potassium hydroxide, and becomes incandescent when moistened with it; melts at a red heat, and volatilises at very high temperatures.

The *Tetroxide*, K_2O_4, or $\begin{array}{c}K—O—O\\ \quad\quad\ \ |\\ K—O—O\end{array}$?, is produced when potassium is burnt in excess of dry air or oxygen gas. It is a chrome-yellow powder which cakes together at about 280°. It absorbs moisture rapidly, and is decomposed by water, giving off oxygen, and forming a solution of the *dioxide*. When gently heated in a stream of carbon monoxide, it yields potassium carbonate and two atoms of oxygen,

$$K_2O_4 + CO = K_2CO_3 + O_2;$$

with carbon dioxide it acts in a similar manner, giving off three atoms of oxygen.—(Harcourt, Chem. Soc. Jour., 1861, p. 267.)

POTASSIUM HYDROXIDE, KHO, commonly called *caustic potash*, or *potassa*, is a very important substance, and one of great practical utility. It is always prepared by decomposing the carbonate with calcium hydroxide (slaked lime).

Experiment.—10 parts of potassium carbonate are dissolved in 100 parts of water, and heated to ebullition in a clean untinned iron, or, still better, silver vessel; 8 parts of good quicklime are meanwhile slaked, and the resulting calcium hydroxide is added, little by little, to the boiling solution of carbonate, with frequent stirring. When

all the lime has been introduced, the mixture is boiled for a few minutes, then removed from the fire and covered up. In a very short time the solution will have become quite clear, and fit for decantation, the calcium carbonate, with the excess of hydrate, settling down as a heavy, sandy precipitate. The solution should not effervesce with acids.

It is essential in this process that the solution of potassium carbonate be dilute, otherwise the decomposition becomes imperfect. The proportion of lime recommended is much greater than that required by theory, but it is necessary to have an excess.

The solution of potassium hydroxide may be concentrated by quick evaporation in the iron or silver vessel to any desired extent: when heated until vapour of water is no longer given off, and then left to cool, it yields the solid hydroxide, KHO. Pure potassium hydroxide is also easily obtained by heating to redness for half an hour in a covered copper vessel, one part of pure powdered nitre with two or three parts of finely-divided copper foil. The mass, when cold, is treated with water.

Potassium hydroxide is a white solid substance, very deliquescent, and soluble in water; alcohol also dissolves it freely, which is the case with comparatively few potassium compounds: the solid hydroxide of commerce, which is very impure, may thus be purified. The solution of this substance possesses, in the very highest degree, the properties termed alkaline: it restores the blue colour to litmus which has been reddened by an acid; neutralises completely the most powerful acids: has a nauseous and peculiar taste; dissolves the skin, and many other organic matters, and is sometimes used by surgeons as a cautery. Its chief use, however, is for the manufacture of soft soap.

Potassium hydroxide, both in the solid state and in solution, rapidly absorbs carbon dioxide from the air: hence it must be kept in closely stopped bottles. When imperfectly prepared, or partially altered by exposure, it effervesces with an acid. It is not decomposed by heat, but volatilises undecomposed at a very high temperature.

The following table of the densities and value in potassium hydroxide of different solutions of caustic potash has been calculated by Gerlach from the experiments of Tunnermann and Schiff:—

KOH per cent.	Density.	KOH per cent.	Density.
1	1·009	40	1·411
5	1·041	45	1·475
10	1·083	50	1·539
15	1·128	55	1·604
20	1·177	60	1·667
25	1·230	65	1·729
30	1·288	70	1·790
35	1·349		

The *liquor potassæ* of the pharmacopœia contains about 5 per cent KOH, and has a density 1·058.

Potassium Chlorate, $KClO_3 = ClO_2(OK)$.—The theory of the production of chloric acid by the action of chlorine gas on a solution of caustic potash, has been already explained (p. 113).

Potassium chlorate is manufactured by passing chlorine gas into milk of lime, so as to form calcium chloride and chlorate. The resulting solution, which has usually a pink colour, due to the formation of a minute quantity of a permanganate from the oxide of manganese present in the lime, is then mixed with potassium chloride and evaporated down. When sufficiently concentrated and allowed to cool, the potassium chlorate crystallises out, leaving calcium chloride with only a small quantity of chlorate in the liquid. It may be purified by one or two recrystallisations.

Potassium chlorate is soluble in about 20 parts of cold and 2 of boiling water: the crystals are anhydrous, flat, and tabular; in taste it somewhat resembles nitre. When heated it gives off the whole of its oxygen as gas and leaves potassium chloride. By arresting the decomposition when the evolution of gas begins to slacken, and redissolving the salt, potassium perchlorate and chloride may be obtained.

This salt deflagrates violently with combustible matter, explosion often occurring by friction or blows. When about 1 grain-weight of chlorate and an equal quantity of sulphur are rubbed in a mortar, the mixture explodes with a loud report: hence it cannot be used in the preparation of gunpowder instead of the nitrate. Potassium chlorate has been for many years a large article of commerce, being employed, together with phosphorus, in making instantaneous-light matches.

Experiments.—Boil some potassium chlorate with about three times its weight of water in a test-tube until dissolved. Allow the solution to cool. When the liquid has crystallised, drain away the solution, rinse the crystals with distilled water, and place them on filter paper to dry. Of these crystals dissolve a little in distilled water and add silver nitrate. No visible change occurs. Heat the dried crystals in a test-tube till oxygen freely escapes, then when cold, boil the mass in a little water and cool the solution. If strong enough it will deposit granular crystals of potassium perchlorate, $KClO_4$. A portion of the liquid tested with solution of silver nitrate will now give a white, curdy precipitate of silver chloride, $AgCl$.

Potassium Perchlorate, $KClO_4 = ClO_3(OK)$.—This salt has been already noticed under the head of perchloric acid, also in the preceding paragraph. It is best prepared by projecting powdered potassium chlorate into warm nitric acid, when the chloric acid is resolved into perchloric acid, chlorine, and oxygen. The salt is separated from the nitrate by crystallisation. Potassium perchlorate is a very slightly soluble salt: it requires 55 parts of cold water, but is more freely taken up by boiling water. The crystals are small, and have the figure of an octahedron with square base. It is decomposed by heat into oxygen and potassium chloride.

Potassium Bromate, $KBrO_3$, is obtained by passing ehlorine into a warm solution of potassium bromide and eaustic potash: $KBr + 6KOH + 3Cl_2 = KBrO_3 + 6KCl + 3H_2O$. The solution on cooling deposits part of the bromate, and the rest may be separated by precipitation with aleohol. It erystallises in six-sided tables or prisms, moderately soluble in hot, very slightly in cold water.

Potassium Iodate, KIO_3, is prepared by passing chlorine into eold water eontaining iodine in suspension till the whole is dissolved, then adding the ealeulated quantity of potassium chlorate and warming: $ICl + KClO_3 = Cl_2 + KIO_3$. It forms small eubie erystals, and requires a mueh stronger heat to deeompose it than the ehlorate. It unites with iodie aeid, forming the salts $KIO_3.HIO_3$ and $KIO_3.2HIO_3$. *Potassium Periodate*, KIO_4, is formed when ehlorine is passed through a mixture of the iodate and eaustie potash, and separates in shining erystals isomorphous with the perehlorate (see *Periodic Acid*, p. 110).

Potassium Sulphates.—Potassium forms a normal or neutral sulphate, two aeid sulphates, and an anhydrosulphate.

Normal Potassium Sulphate, or *Dipotassic Sulphate*, $K_2SO_4 = SO_2(OK)_2 = K_2O,SO_3$, is obtained by neutralising with potassium carbonate the aeid residue left in the retort after the preparation of nitrie aeid. The solution yields, on eooling, hard transparent crystals of the normal sulphate, whieh may be redissolved in boiling water, and reerystallised.

Potassium sulphate is soluble in about 10 parts of cold, and in a mueh smaller quantity of boiling water: it has a bitter taste, and is neutral to test-paper. The erystals are combinations of rhombie pyramids and prisms, much resembling those of quartz in figure and appearanee; they are anhydrous, and deerepitate when suddenly heated, whieh is often the ease with salts eontaining no water of erystallisation. They are quite insoluble in aleohol.

Acid Potassium Sulphate, *Hydrogen and Potassium Sulphate*, or *Monopotassic Sulphate*, $KHSO_4 = SO_2(OK)(OH)$, eommonly ealled *Bisulphate of Potash.*—To obtain this salt, the normal sulphate in powder is mixed with half its weight of oil of vitriol, and the whole evaporated to dryness in a platinum vessel placed under a chimney: the fused salt is dissolved in hot water and left to crystallise. The crystals have the figure of flattened rhombic prisms, and are much more soluble than the normal salt, requiring only twiee their weight of water at 15·5°, and less than half that quantity at 100°. The solution has a sour taste and strongly aeid reaction.

Potassium Disulphate or *Pyrosulphate*, $K_2S_2O_7$, derived from Nordhausen sulphurie aeid, $H_2S_2O_7$, and eommonly ealled *anhydrous bisulphate of potash*, is obtained by dissolving equal weights of the normal sulphate and oil of vitriol in a small quantity of warm distilled water, and leaving the solution to eool.

The pyrosulphate erystallises out in long delieate needles, which

if left for several days in the mother-liquor, disappear, and give place to crystals of the ordinary acid sulphate above described. This salt is decomposed by a large quantity of water, and is converted by strong fuming sulphuric acid into *hydropotassic pyrosulphate*, KHS_2O_7, which crystallises in transparent prisms. The normal pyrosulphate in fine powder, heated with an alcoholic solution of potassium hydrosulphide, is converted into sulphate and thiosulphate, with evolution of hydrogen sulphide:

$$K_2S_2O_7 + 2KHS = K_2SO_4 + K_2S_2O_3 + H_2S.$$

Potassium Nitrate; *Nitre; Saltpetre*, $KNO_3 = NO_2(OK)$.—This important compound is a natural product, being disengaged by a kind of efflorescence from the surface of the soil in certain dry and hot countries. It is now known that the conversion of the nitrogen of decomposing organic matters in the soil into nitrate is accomplished through the agency of two micro-organisms, one of which causes the oxidation to proceed only as far as the production of nitrite, the other effecting the further oxidation of the nitrite to nitrate.

The natural process which goes on everywhere but is most rapid in warm climates has, for the last hundred years, been imitated artificially in several European countries.

In France and Germany large quantities of artificial nitre are prepared by mixing animal refuse of all kinds with old mortar or slaked lime and earth, and placing the mixture in heaps, protected from the rain by a roof, but freely exposed to the air. From time to time the heaps are watered with putrid urine, and the mass is turned over, to expose fresh surfaces to the air. When much salt has been formed, the mixture is lixiviated, and the solution, which contains calcium nitrate, is mixed with potassium carbonate; calcium carbonate is precipitated and potassium nitrate left in solution. The filtered solution is then made to crystallise, and the crystals are purified by re-solution and crystallisation, the liquid being stirred to prevent the formation of large crystals.

A large portion of the nitre used in this country comes from India: it is dissolved in water, a little potassium carbonate is added to precipitate lime, and then the salt is purified as above.

Considerable quantities of nitre are now manufactured by decomposing native sodium nitrate (Chili saltpetre) with carbonate or chloride of potassium. In Belgium the potassium carbonate obtained from the ashes of the beetroot sugar manufactories is largely used for this purpose.

Potassium nitrate usually crystallises in anhydrous six-sided prisms, with dihedral summits, belonging to the rhombic or trimetric system: it is soluble in 7 parts of water at 15·5°, and in its own weight of boiling water. Its taste is saline and cooling, and it is without action on vegetable colours. It melts at a temperature below redness, and is completely decomposed by a strong heat.

When deposited from hot solutions, potassium nitrate forms

rhombohedrons isomorphous with those of sodium nitrate. These crystals change into the ordinary prisms if broken or touched with a crystal of common nitre.

When it is thrown on the surface of many metals in a state of fusion, or mixed with combustible matter and heated, rapid oxidation ensues, at the expense of the oxygen of the salt. Examples of such mixtures are found in common black gunpowder, and in nearly all pyrotechnic compositions, which burn in this manner independently of the oxygen of the air, and even under water. Gunpowder is made by very intimately mixing together potassium nitrate, charcoal, and sulphur, in proportions which approach 2 molecules of nitre, 3 atoms of carbon, and 1 atom of sulphur.

These quantities give, reckoned to 100 parts, and compared with the proportions used in the manufacture of the English Government powder, the following results :—

	Theory.	Proportions in Practice.
Potassium nitrate, . . .	74·8	75
Charcoal, ...	13·3	15
Sulphur, ...	11·9	10
	100·0	100

The nitre is rendered very pure by the means already mentioned, freed from water by fusion, and ground to fine powder ; the sulphur and charcoal—the latter being made from light wood, as dogwood or alder—are also finely ground, after which the materials are weighed out, moistened with water, and thoroughly mixed by grinding under an edge-mill. The mass is then subjected to great pressure, and the mill-cake thus produced is broken in pieces, and placed in sieves made of perforated vellum, moved by machinery, each containing, in addition, a round piece of heavy wood. The grains of powder broken off by attrition fall through the holes in the skin, and are easily separated from the dust by sifting. The powder is, lastly, dried by exposure to steam-heat, and sometimes glazed or polished by agitation in a kind of cask mounted on an axis.

It was formerly supposed that when gunpowder is fired, the whole of the oxygen of the potassium nitrate was transferred to the carbon, forming carbon dioxide, the sulphur combining with the potassium, and the nitrogen being set free. There is no doubt that this reaction does take place to a considerable extent, and that the large volume of gas thus produced, and still further expanded by the very high temperature, sufficiently accounts for the explosive effects. But investigations by Bunsen, Karolyi, and others have shown that the actual products of the combustion of gunpowder are much more complicated than this theory would indicate, a very large number of products being formed, and a considerable portion of the oxygen being transferred to the potassium sulphide, converting it into sulphate, which in fact constitutes the chief portion of the solid residue and of the smoke formed by the explosion.

Experiments.—1. Place in an evaporating dish half a pint of water, heat over a lamp till boiling, and add about two ounces of nitre and an ounce of common salt. Boil the solution till reduced by evaporation to about one-fourth, then remove the lamp, and carefully pour off the still hot solution into a smaller dish, leaving the crystalline deposit of common salt behind. The sodium chloride may thus be separated, from the fact that its solubility in boiling water is very little greater than in cold water. The potassium nitrate is deposited in long prisms from the concentrated solution on cooling.

2. Mix, by grinding in a mortar, about 4 grams of nitre with 1 gram of charcoal. Place the mixture on a tile or iron tray, and apply a flame. When the deflagration is over, dissolve the residue (chiefly K_2CO_3) in water, and add an acid. Observe that carbon dioxide escapes with effervescence.

Potassium Phosphates.—The *Normal Orthophosphate*, K_3PO_4, formed by igniting phosphoric acid with excess of potassium carbonate, is easily soluble in water, and crystallises in small needles. The *dipotassic salt*, K_2HPO_4, obtained by mixing aqueous phosphoric acid with a quantity of hydroxide or carbonate of potassium sufficient to produce a slight alkaline reaction, and evaporating, is easily soluble in water, and uncrystallisable. The *monopotassic salt*, KH_2PO_4, obtained by using a slight excess of phosphoric acid, forms small needle-shaped crystals, belonging to the quadratic system, easily soluble in water, insoluble in alcohol.

Normal Potassium Pyrophosphate, $K_4P_2O_7$, formed by igniting dipotassic orthophosphate, is deliquescent, and separates from aqueous solution in fibrous crystals containing $3H_2O$. The *acid salt*, $K_2H_2P_2O_7$, separates as a deliquescent mass on adding alcohol to a solution of the normal pyrophosphate in acetic acid.

Potassium Monometaphosphate, KPO_3, obtained by igniting monopotassic orthophosphate, is almost insoluble in water. The *dimetaphosphate*, $K_2P_2O_6,H_2O$, prepared by decomposing the corresponding copper salt with potassium sulphide, is soluble in water, and crystallisable ; it is converted by ignition into the monometaphosphate.

Potassium Arsenates.—The *normal salt*, K_3AsO_4, obtained by treating arsenic acid with excess of potash, is crystalline. The *dipotassic salt*, K_2HAsO_4, is difficult to crystallise. The *monopotassic salt*, KH_2AsO_4, forms large crystals.

Potassium Arsenites.—The salt, $KAsO_2,H_3AsO_3$, is obtained as a crystalline powder on adding alcohol to a solution of arsenious oxide in the minimum quantity of potash. This salt, heated with solution of potassium carbonate, is converted into the *meta-arsenite*, $KAsO_2$, and this latter heated with caustic potash yields the *diarsenite*, $K_4As_2O_5$, likewise precipitable by alcohol.

A solution of potassium arsenite, known in medicine as "Fowler's solution," is prepared by boiling 1 part arsenious oxide and 1 part

potassium carbonate in distilled water, and diluting to 100 parts of solution.

Borates.—The *metaborate*, KBO_2, obtained by fusing a mixture of boric acid and potassium carbonate in the requisite proportions, is slightly soluble in water, and separates in small monoclinic crystals. It has an alkaline reaction, and absorbs carbonic acid from the air, being thereby converted into the *pyroborate* or *tetraborate*, $K_2B_4O_7 = K_2O,2B_2O_3$. This latter, which is also formed on mixing a solution of boric acid with a slight excess of potash, is easily soluble, and crystallises in hexagonal prisms containing $5H_2O$. The *triborate*, $2KB_3O_5,5H_2O$, or $K_2O,3B_2O_3,5H_2O$, is formed on mixing the hot solutions of boric acid (1 molecule) and potassium carbonate (2 molecules), and separates in glittering rhombic crystals. The *pentaborate*, $KB_5O_84H_2O$ or $K_2O,5B_2O_3,4H_2O$, separates in rhombic octahedrons from a hot solution of caustic potash saturated with boric acid.

Silicates.—The *metasilicate*, K_2SiO_3 or K_2O,SiO_2, is formed when silica is fused with the calculated quantity of potassium carbonate, or with any larger quantity: for experiment shows that one molecule of silica cannot decompose more than one molecule of potassium carbonate, so that, for example, the reaction $2(K_2O,CO_2) + SiO_2 = 2K_2O,SiO_2 + 2CO_2$, cannot take place, and the orthosilicate K_4SiO_4 cannot be thus formed. The *tetrasilicate*, $K_2Si_4O_9$ (Fuchs's soluble glass), is prepared by fusing 45 parts quartz, 30 potashes, and 3 powdered charcoal, boiling the resulting greyish-black glass with water, mixing the concentrated solution with strong alcohol, and washing the precipitate thereby formed with a little cold water. The potash water-glass thus obtained is soluble in water, and may be used for the same purposes as soda water-glass (p. 359), but is now superseded by the latter.

Potassium Fluosilicate or *Silicofluoride*, K_2SiF_6, is precipitated on adding hydrofluosilicic acid to a soluble potassium salt, as a semi-transparent mass, which, after washing and drying, forms a fine white powder, sparingly soluble in cold, freely in hot water. By slow cooling it may be obtained in shining octahedrons.

Potassium Carbonates.—Potassium forms two well-defined carbonates, namely, a normal or neutral carbonate, K_2CO_3, and a hydrogen salt containing $KHCO_3$.

Normal Potassium Carbonate, or *Dipotassic Carbonate*, $K_2CO_3 = CO(OK)_2 = K_2O,CO_2$.—Potassium salts of vegetable acids are of constant occurrence in plants, in the economy of which they perform important functions. The potassium is derived from the soil, which, when capable of supporting vegetable life, always contains that substance. When plants are burned, the organic acids are destroyed, and the potassium is left in the state of carbonate. Wood ashes yield a considerable proportion of the potash of commerce.

The great natural depository of the alkali is the felspar of granitic and other unstratified rocks, where it is combined with silica, and in an insoluble state. The extraction thence is attended with great difficulties, but the extraction of potash from felspathic rocks is a matter of smaller importance since the discovery and utilisation of the immense deposits of salt at Stassfurt (see *Potassium Chloride*). There are, however, natural processes at work, by which potash is constantly being eliminated from these rocks. Under the influence of atmospheric carbonic acid and water, the rocks disintegrate into soils, and as the alkali acquires solubility, it is gradually taken up by plants, and accumulates in their tissues chiefly in the form of organic salts.

Potassium-salts are always most abundant in the green and tender parts of plants, as may be expected, since from these, evaporation of nearly pure water takes place to a large extent: the solid timber of forest trees contains comparatively little.

In preparing the salt on an extensive scale, the ashes are subjected to a process called *lixiviation*: they are put into a large cask or tun, having, near the bottom, an aperture stopped by a plug, and a quantity of water is added. After some hours the liquid is drawn off, and more water added, that the whole of the soluble matter may be removed. The weakest solutions are poured in place of water upon fresh quantities of ash. The solutions are then evaporated to dryness, and the residue is calcined, to remove a little brown organic matter: the product is the crude potash or pearlash of commerce, of which very large quantities are obtained from Russia and America. The salt is very impure, containing potassium silicate, sulphate, chloride, &c.

Of late years, the native potassic chloride from the Stassfurt salt-mines has been largely utilised for the production of the carbonate by a process which is identical with the Le Blanc or "black ash" process for the production of sodium carbonate (p. 362), substituting potassium chloride for sodium chloride.

The purified potassium carbonate of pharmacy is prepared from the crude article by adding an equal weight of cold water, agitating and filtering, most of the foreign salts, from their inferior solubility, being left behind. The solution is then boiled down to a very small bulk, and left to cool, when the carbonate separates in small crystals containing 2 molecules of water, $K_2CO_3,2H_2O$; these are drained from the mother-liquor, and then dried in a stove.

A still purer salt may be obtained by exposing to a red heat purified cream of tartar (acid potassium tartrate), and separating the carbonate by solution in water and crystallisation, or evaporation to dryness.

Potassium carbonate is extremely deliquescent, and soluble in less than its own weight of water; the solution is highly alkaline to test paper. It is insoluble in alcohol. By heat the water of crystallisation is driven off, and by a temperature of full ignition the salt is fused, but not otherwise changed. This substance is largely used in the arts, and is a compound of great importance.

Acid Potassium Carbonate, Hydrogen and Potassium Carbonate, or *Monopotassic Carbonate*, $KHCO_3$; commonly called *Bicarbonate of Potash.*—When a stream of carbonic acid gas is passed through a cold solution of normal potassium carbonate, the gas is rapidly absorbed, and a white, crystalline, less soluble substance separated, which is the acid salt. It is collected, drained, redissolved in warm water, and the solution is left to crystallise.

Potassium hydrogen carbonate is much less soluble than the normal carbonate, requiring 4 parts of cold water to dissolve it. The solution is only slightly alkaline to test-paper, and has a much milder taste than the normal salt. When boiled it gives off carbon dioxide. The crystals, which are large and beautiful, derive their form from a monoclinic prism: they are decomposed by heat, water and carbon dioxide being evolved, and normal carbonate left behind:

$$2KHCO_3 = K_2CO_3 + H_2O + CO_2.$$

Potassium Sulphides.—Potassium heated in sulphur vapour burns with great brilliancy. It unites with sulphur in five different proportions, forming the compounds K_2S, K_2S_2, K_2S_3, K_2S_4, K_2S_5; also a hydrosulphide or sulphydrate, KHS.

Monosulphide, K_2S.—It is doubtful whether this compound has been obtained in the pure state. It is commonly said to be produced by heating potassium sulphate in a current of dry hydrogen, or by igniting the same salt in a covered vessel with finely divided charcoal; but, according to Bauer, one of the higher sulphides is always formed at the same time, together with oxide of potassium. The product has a reddish-yellow colour, is deliquescent, and acts as a caustic on the skin. When potassium sulphate is heated in a covered crucible with excess of lamp-black, a mixture of potassium sulphide and finely divided carbon is obtained, which takes fire spontaneously on coming into contact with the air. The monosulphide might perhaps be obtained pure by heating 1 molecule of potassium sulphydrate, KHS, with 1 atom of the metal.

When sulphydric acid gas is passed to saturation into a solution of caustic potash, a solution of the sulphydrate is obtained, which is colourless at first, but if exposed to the air, quickly absorbs oxygen and turns yellow, in consequence of the formation of bisulphide:

$$2KHS + O = K_2S_2 + H_2O.$$

If a solution of potash be divided into two parts, one half saturated with hydrogen sulphide, and then mixed with the other, a solution is formed which may contain potassium monosulphide:

$$KHS + KHO = K_2S + H_2O.$$

But it is also possible that the hydroxide and hydrosulphide may mix without mutual decomposition. The solution, when mixed with one of the stronger acids, gives off hydrogen sulphide without deposition of sulphur, a reaction which is consistent with either view of its constitution.

The *bisulphide*, K_2S_2, is formed, as already observed, on exposing a solution of the hydrosulphide to the air till it begins to show turbidity. By evaporation in a vacuum, it is obtained as an orange-coloured, easily fusible substance.

The *trisulphide*, K_2S_3, the *tetrasulphide*, K_2S_4, and the pentasulphide are components of the mixture known as *liver of sulphur.*

The *pentasulphide*, K_2S_5, is formed by boiling a solution of any of the preceding sulphides with excess of sulphur till it is saturated, or by fusing either of them in the dry state with sulphur. The excess of sulphur then separates and floats above the dark brown pentasulphide.

Liver of sulphur, or *hepar sulphuris*, is a name given to a brownish substance, sometimes used in medicine, made by fusing together different proportions of potassium carbonate and sulphur. It is a variable mixture of the higher sulphides with thiosulphate and sulphate of potassium.

When equal parts of sulphur and dry potassium carbonate are melted together at a temperature not exceeding 250°, the decomposition of the salt is quite complete, and all the carbon dioxide is expelled. The fused mass dissolves in water, with the exception of a little mechanically mixed sulphur, with dark brown colour, and the solution is found to contain nothing beside pentasulphide and thiosulphate of potassium :

$$3K_2O + S_{12} = 2K_2S_5 + K_2S_2O_3 .$$

When the mixture has been exposed to a temperature approaching that of ignition, it is found, on the contrary, to contain potassium sulphate, arising from the decomposition of the thiosulphate which then occurs :

$$4K_2S_2O_3 = K_2S_5 + 3K_2SO_4 .$$

From both these mixtures the potassium pentasulphide may be extracted by alcohol, in which it dissolves.

When the carbonate is fused with half its weight of sulphur only, the trisulphide is produced, as above indicated, instead of the pentasulphide.

The effects described happen in the same manner when potassium hydroxide is substituted for the carbonate ; also, when a solution of the hydroxide is boiled with sulphur, a mixture of sulphide and thiosulphate always results.

Potassium-salts are colourless when not associated with a coloured metallic oxide or acid. They are all more or less soluble in water, and may be distinguished by the following characters :—

1. Solution of *tartaric acid*, added in excess to a moderately strong solution of a potassium salt, gives, after some time, a white crystalline precipitate of cream of tartar, $KHC_4H_4O_6$; the effect is greatly promoted by strong agitation.

2. Solution of *platinic chloride*, with a little hydrochloric acid, if

necessary, gives, under similar conditions, a crystalline yellow precipitate, which is a double salt of platinum tetrachloride and potassium chloride, $2KCl.PtCl_4$. Both this compound and cream of tartar are, however, soluble in about 110 parts of cold water. An addition of alcohol increases the delicacy of both tests.

3. *Perchloric acid*, and *Silicofluoric acid*, added to a potassium-salt, give rise to slightly soluble white precipitates.

4. Picric acid, $HC_6H_2(NO_2)_3$, dissolved in proof spirit when added in slight excess to aqueous solutions of potassium salts gives a yellow crystalline precipitate of potassium picrate, $KC_6H_2(NO_2)_3$.

5. A mixture of sodium nitrite and cobalt nitrate dissolved in water and acidified with acetic acid gives, when added to a solution of a potassium salt, a precipitate of cobalt yellow forming slowly in dilute solutions.

6. Potassium salts usually colour the outer blow-pipe flame purple or violet; this reaction is clearly perceptible only when the potassium salts are pure.

7. The spectral phenomena exhibited by potassium compounds are mentioned at page 333, and shown in the coloured plate facing the title-page.

SODIUM.

Symbol, Na (Natrium). Atomic weight, 23.

Sodium is a very abundant element, and very widely diffused. It occurs in large quantities as chloride, in rock-salt, sea-water, salt-springs, and many other mineral waters; more rarely as carbonate, borate, and sulphate, in solution, or in the solid state, and as silicate in many minerals.

Metallic sodium was obtained by Davy soon after the discovery of potassium, and by similar means. Gay-Lussac and Thenard afterwards prepared it by decomposing sodium hydroxide with metallic iron at a white heat; and Brunner showed that it may be prepared with much greater facility by distilling a mixture of sodium carbonate and charcoal.

The preparation of sodium by this last-mentioned process is much easier than that of potassium, not being complicated, or only to a slight extent, by the formation of secondary products.

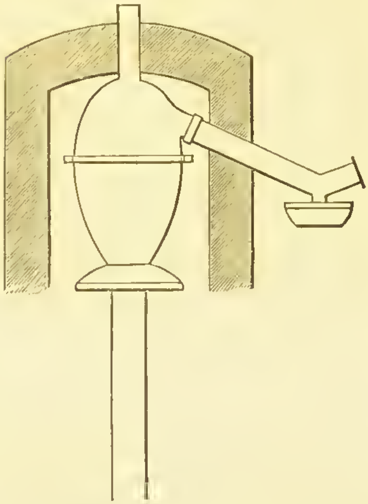
The distillation is performed, on the laboratory scale, in a mercury bottle heated exactly in the manner described for the preparation of potassium. For manufacturing operations, the mixture is introduced into iron cylinders, which are heated in a reverberatory furnace, and so arranged that, at the end of the distillation, the exhausted charge may be withdrawn and a fresh-charge introduced, without displacing the cylinders or putting out the fire. The receivers used in either case are the same in form and dimensions as those employed in the preparation of potassium.

When the process goes on well, the sodium collected in the

receivers is nearly pure ; it may be completely purified by melting it under a thin layer of petroleum. This liquid is decanted as soon as the sodium becomes perfectly fluid, and the metal is run into moulds like those used for casting lead or zinc.

By the process just described less than half the sodium contained in the charge distils over, and the method is now superseded by a process introduced by Mr H. Y. Castner, which is based on the decomposition of fused caustic soda, by a compound or intimate mixture of metallic iron and carbon. The latter is prepared by heating peroxide of iron (purple ore) in reducing gas, whereby spongy metallic iron is obtained, and this is subsequently mixed with pitch and coked. The resulting metallic carbonide is mixed with caustic soda in a steel crucible, and the crucible, after a preliminary heating of its contents, is placed upon a support within the furnace, shown in the figure, and is then raised till its mouth is in firm contact with a cover provided with a tube for carrying off the hydrogen and vapours of the metal which are evolved. The cover and condensing-tube are fixed, whilst successive crucibles with their charges can be brought into position and the metal distilled off. The change which occurs is represented by the following equation :—

Fig. 123.



$$6NaHO + Fe + C_2 = 2Na_2CO_3 + 3H_2 + Fe + Na_2.$$

Sodium is a silver-white metal, greatly resembling potassium in every respect. Its density is 0·972. It is soft at common temperatures, melts at 97·6°, and oxidises very rapidly in the air. When placed on the surface of cold water, it decomposes that liquid with great violence, but seldom takes fire unless the motions of the fragment are restrained, and its rapid cooling is diminished by adding gum or starch to the water. With hot water it takes fire at once, burning with a bright yellow flame, and producing a solution of soda.

Experiment.—Drop a piece of sodium, half the size of a pea, into cold water, using the same precautions as in the case of potassium. The sodium melts, forming a spherical globule, from which hydrogen escapes. Apply a lighted match ; the hydrogen will burn with a yellow flame. Test the liquid with red litmus paper.

Sodium Chloride; Common Salt, $NaCl$.—This very important substance is found in many parts of the world in solid beds or

irregular strata of immense thickness, as in Cheshire, Spain, Galicia, at Stassfurt, and many other localities. An inexhaustible supply exists also in the waters of the ocean, and large quantities are obtained from saline springs.

Salt is obtained from sea-water by evaporation in salterns or brine-pans, with the aid of air and sunshine. This process is extensively practised on the coasts of France, Spain, and Portugal, as it was formerly in this country, at Hayling Island, near Portsmouth; at Lymington, in Dorsetshire; and in Scotland, at Saltcoats, on the Ayrshire coast. The salt thus prepared is called bay-salt; the mother-liquor, called *bittern*, contains the sulphates, chlorides, and bromides of magnesium and potassium, and is utilised as a source of bromine.

Rock-salt is sometimes mined and brought to the surface in the solid state, but generally speaking it is too impure for use. It is therefore more usual to form an artificial brine-well by sinking a shaft into the rock-salt, and, if necessary, introducing water. This when saturated is pumped up, and evaporated more or less rapidly in large iron pans. As the salt separates, it is removed from the bottom of the vessel by means of a scoop, pressed while still moist into moulds, and then transferred to the drying-stove. When large crystals are required, as for the coarse-grained salt used in curing provisions, the evaporation is slowly conducted. Common salt is apt to be contaminated with sodium sulphate, calcium sulphate, and magnesium chloride, the last of which renders it liable to become damp in the air. These impurities may be removed by passing hydrochloric acid gas into a saturated and filtered solution of the salt, whereby pure sodium chloride is precipitated, the other salts remaining in solution. The precipitate is washed on a filter with strong hydrochloric acid, then dried at a high temperature in a platinum basin.

Sodium chloride, when pure, is not deliquescent in moderately dry air. It crystallises in anhydrous cubes, which are often grouped together into pyramids, or steps. It requires about $2\frac{1}{2}$ parts of water at 15° for solution, and its solubility is only slightly increased by heat; it dissolves to some extent in spirit of wine, but is nearly insoluble in absolute alcohol. It melts at a red heat, and volatilises at a still higher temperature. The economical uses of common salt are well known.

The *iodide* and *bromide of sodium* much resemble the corresponding potassium-compounds; they crystallise in cubes, which are anhydrous, and very soluble in water.

Sodium Oxide.—Sodium forms a monoxide and a dioxide; also a hydroxide corresponding with the former.

Sodium Monoxide, or *Anhydrous Soda*, Na_2O, is produced together with the dioxide, when sodium burns in the air, and may be obtained pure by exposing the dioxide to a very high temperature. It is a grey mass, which melts at a red heat, and volatilises with difficulty.

Sodium Hydroxide, or *Caustic Soda*, NaHO. — This substance is prepared by decomposing a somewhat dilute solution of sodium

carbonate with calcium hydroxide : the description of the process employed in the case of potassium hydroxide, and the precautions necessary, apply word for word to that of sodium hydroxide.

The solid hydroxide is a white fusible substance, very similar in properties to potassium hydroxide. It is deliquescent, but dries up again after a time, in consequence of the absorption of carbon dioxide. The solution is highly alkaline, and a powerful solvent for animal matter : it is used in large quantity for making soap.

The strength of a solution of caustic soda may be determined from a knowledge of its density, by the aid of the following table drawn up by Schiff :—

NaOH per cent.	Density.	NaOH per cent.	Density.
1	1·012	35	1·384
5	1·059	40	1·437
10	1·115	45	1·488
15	1·170	50	1·540
20	1·225	55	1·591
25	1·279	60	1·643
30	1·332		

Sodium Dioxide, Na_2O_2, formed by heating sodium to about 200° in a current of dry air, is white at ordinary temperatures, but becomes yellow when heated. It dissolves in water without decomposition. The solution may be evaporated under reduced pressure, depositing crystalline plates having the composition $Na_2O_2,8H_2O$. These crystals left to effloresce over oil of vitriol for nine days lose three-fourths of their water, and yield another hydrate containing $Na_2O_2,2H_2O$. The aqueous solution of sodium dioxide when heated on the water-bath, is decomposed into oxygen and the monoxide. The dioxide is now an article of commerce, and is used in analytical processes as an oxidising agent.

Sodium Hypochlorite, $NaOCl$, is contained, together with the chloride, in the bleaching liquid (formerly known as chloride of soda, or *Eau de Labarraque*), obtained by passing chlorine into a cold solution of caustic soda.

Sodium Chlorate, $NaClO_3$, obtained by neutralising sodium carbonate with chloric acid, or by boiling 9 parts of potassium chlorate with 7 parts sodium silicofluoride, crystallises on cooling in regular tetrahedrons. It is much more soluble than potassium chlorate, 100 parts of water dissolving 81·9 parts of it at 0°, and 232·6 parts at 100°. Its great solubility renders it very useful to the calico-printer in the production of aniline-black.

Sodium Hyposulphite, $NaHSO_2$, is formed by the deoxidising action of zinc on the sulphite. Its preparation has already been described (p. 136). It crystallises in needles, soluble in water and in weak spirit, the solution exhibiting strong bleaching and reduc-

ing properties : hence it is used as a reducing agent for indigo, and for the estimation of oxygen.

Sodium Sulphites.—The *normal salt*, Na_2SO_3, obtained by saturating a solution of sodium carbonate with sulphur dioxide, and then adding an equal quantity of the carbonate, crystallises in transparent, monoclinic prisms, which contain 7 molecules of water, and give up the whole of it at 150°. The solution has a sharp taste and alkaline reaction. The *acid salt*, $NaHSO_3$, separates from a cold solution of sodium carbonate saturated with sulphur dioxide in turbid crystals, and is precipitated from its aqueous solution by alcohol as a white powder.

Sodium Sulphates.—The *normal salt*, Na_2SO_4, is a bye-product in many chemical operations and an intermediate product in the manufacture of the carbonate (see p. 362) : it may of course be prepared directly, if wanted pure, by adding dilute sulphuric acid, to saturation, to a solution of sodium carbonate. It crystallises in forms derived from an oblique rhombic prism. The crystals, commonly called *Glauber's salt*, contain 10 molecules of water, are efflorescent, and undergo watery fusion when heated, like those of the carbonate ; they are soluble in twice their weight of cold water, and rapidly increase in solubility as the temperature of the liquid rises to 34°, at which point the salt becomes indefinitely soluble (see fig. 43, p. 80). When the salt is heated beyond this point, the solubility diminishes, and a portion of anhydrous sulphate is deposited. A warm saturated solution evaporated at a high temperature deposits opaque prismatic crystals, which are anhydrous. The salt has a slight bitter taste, and is purgative. Mineral springs sometimes contain it, as, for example, the springs at Cheltenham.

Experiments with Glauber's salt have been described, p. 82.

Sodium and Hydrogen Sulphate, or *Acid Sodium Sulphate*, $2NaHSO_4,3H_2O$ or $Na_2SO_4,H_2SO_4,3H_2O$, commonly called *Bisulphate of Soda*, is prepared by adding to 10 parts of the anhydrous normal sulphate, 7 of oil of vitriol, evaporating the whole to dryness, and gently heating till water vapour ceases to be given off. The acid sulphate is very soluble in water, and has an acid reaction. It is not deliquescent. When very strongly heated the fused salt gives up sulphuric oxide, and is converted into normal sulphate ; a change which necessarily supposes the previous formation of a pyrosulphate, $Na_2S_2O_7$ or Na_2SO_4,SO_3.

Sodium Thiosulphate, $Na_2S_2O_3$, formerly called *Hyposulphite.*—This salt is formed from the sulphite, Na_2SO_3, by addition of sulphur. There are several modes of preparing it. One is to heat gently a solution of normal *sodium sulphite* with sulphur during several days. By careful evaporation at a moderate temperature the salt is obtained in large regular crystals, which are very soluble in water. It is usually manufactured from alkali waste, which consists chiefly of calcium monosulphide (see p. 366). This is sus-

pended in water, sulphur dioxide passed into the liquid, and the calcium salt converted into the sodium salt by precipitation with sodium carbonate or sulphate. It is much used in photography as a solvent for the unaltered silver chloride, and bromide, and in paper-manufacture as an antichlor.

Sodium Nitrate, $NaNO_3$.—This salt, sometimes called *Cubic Nitre*, or *Chili Saltpetre*, occurs native, and in enormous quantity, at Tarapaca in Southern Peru, where it forms a regular bed, of great extent, along with gypsum, common salt, and remains of recent shells. The pure salt commonly crystallises in rhombohedrons, resembling those of calcareous spar. It is deliquescent, and very soluble in water. Sodium nitrate is employed for making nitric acid, but cannot be used for gunpowder, as the mixture burns too slowly, and becomes damp in the air. It is used extensively in agriculture as a superficial manure or top-dressing ; also for preparing potassium nitrate.

Experiment.—Dissolve in the same portion of water contained in an evaporating dish, 18 grams of sodium nitrate and 16 grams of potassium chloride. Evaporate the solution as described under the head of potassium nitrate, and decant the concentrated solution from the crystalline deposit. The solution on cooling shoots into long prisms of potassium nitrate, easily distinguishable from the short rhombohedral crystals of the sodium salt.

Sodium Phosphates.—The chemical relations of these salts have already been explained in speaking of the basicity of acids (pp. 319–320).

1. ORTHOPHOSPHATES. — *Hydrodisodic Phosphate* or *Disodium Orthophosphate*, *Ordinary Phosphate of Soda*, $Na_2HPO_4,12H_2O$, is prepared by precipitating the acid calcium phosphate (obtained in decomposing bone ash with sulphuric acid) with a slight excess of sodium carbonate, and evaporating the clear liquid. It crystallises in large, transparent, monoclinic prisms, which are efflorescent, dissolve in 4 parts of cold water, and at a higher temperature give off water, and are converted into metaphosphate. The salt is bitter and purgative ; its solution is alkaline to test-paper. The salt also crystallises from a hot solution in prisms which contain $7H_2O$.—*Trisodium orthophosphate*, $Na_3PO_4,12H_2O$, is obtained by adding a solution of caustic soda to the preceding salt. The crystals are slender six-sided prisms, soluble in 5 parts of cold water. It is decomposed by acids, even carbonic, but suffers no change by heat except the loss of its water of crystallisation. Its solution is strongly alkaline.—*Monosodium orthophosphate*, NaH_2PO_4,H_2O, formerly called superphosphate or biphosphate, may be obtained by adding phosphoric acid to the ordinary phosphate, until it ceases to precipitate barium chloride, and exposing the concentrated solution to cold. The crystals are prismatic, very soluble, and have an acid reaction. When strongly heated, this salt gives off water and is converted into metaphosphate (*infra*).

2. *Pyrophosphates.*—The *normal pyrophosphate*, $Na_4P_2O_7,10H_2O$, is

obtained as an anhydrous colourless vitreous mass by igniting disodic orthophosphate, and crystallises from aqueous solution in monoclinic prisms. The solution is alkaline. The salt is converted into orthophosphate on adding an acid to its aqueous solution.—The *acid pyrophosphate*, $Na_2H_2P_2O_7$ is obtained by heating disodic orthophosphate to 150° with strong hydrochloric acid, or by heating monosodic orthophosphate to 190–204°: $2NaH_2PO_4 = H_2O + Na_2H_2P_2O_7$; also by dissolving the normal pyrophosphate and precipitating with alcohol. This last process yields it as a white crystalline powder. It is easily soluble in water, and forms an acid solution.

Metaphosphates, $nNaPO_3$ (Mono-, Di-, Tri-, etc., p. 321).—$NaPO_3$ is formed by heating sodium hydroxide with a slight excess of phosphoric acid; by heating dihydrosodic orthophosphate to redness for a short time; and by fusing 2 parts sodium nitrate with 1 part of syrupy phosphoric acid. It is insoluble in water, but dissolves in acids, and is converted into orthophosphate by boiling with caustic soda. $Na_2P_2O_6 + 2H_2O$, obtained by boiling the corresponding copper-salt with sodium sulphide, crystallises in slender needles, soluble in 7·2 parts of water. It has a strong tendency to form double salts, *e.g.*, $NaKP_2O_6,H_2O$, which crystallises from a mixed solution of the two simple salts.—$Na_3P_3O_9,6H_2O$ may be prepared by exposing microcosmic salt, $Na(NH_4)HPO_4,4H_2O$, to a moderate heat, or by leaving the same salt in a state of fusion to cool slowly. It dissolves in 4·5 parts of cold water, and separates on spontaneous evaporation in large triclinic prisms.—$Na_4P_4O_{12}$, prepared by decomposing the corresponding lead-salt with sodium sulphide, forms a thick gummy solution, and remains on evaporation as a transparent colloidal mass.—$Na_6P_6O_{18}$ is prepared by fusing either dihydric orthophosphate or microcosmic salt, and cooling the fused mass as quickly as possible, as otherwise the tetrametaphosphate may be formed. It dissolves easily in water and in alcohol, and remains on evaporation at 38° as a gummy mass. The aqueous solution is not altered by boiling with caustic soda.

Experiments on the mutual transformations of the common, meta-, and pyrophosphates.—1. Dissolve in separate portions of water some common phosphate of sodium, $Na_2HPO_4,12H_2O$, and microcosmic salt, $NaNH_4HPO_4$, $4H_2O$; add solution of silver nitrate to each, and observe that they give the same yellow precipitate of silver phosphate, Ag_3PO_4.

2. Make an ounce or two of trisodium phosphate by dissolving common phosphate of sodium in solution of caustic soda, and crystallising the salt. Drain the crystals, redissolve a small portion in water, and test with silver nitrate. The same yellow phosphate is thrown down.

3. Heat about a gram of each of these sodium salts in a porcelain crucible or on platinum foil to low redness. Redissolve the residue in water, and test the solution with nitrate of silver.

The trisodium salt is unchanged by heat, and gives yellow triargentic phosphate.

Disodium phosphate gives pyrophosphate, $Na_4P_2O_7$, and the solution of this compound gives a white precipitate of silver pyrophosphate, $Ag_4P_2O_7$.

Monosodium phosphate and microcosmic salt leave a residue of a metaphosphate $(NaPO_3)_n$, which gives with silver nitrate a translucent white precipitate of silver metaphosphate $(AgPO_3)_n$.

4. Dissolve the residues of pyro- and metaphosphate of sodium in water, acidify with hydrochloric acid, boil for about an hour, then evaporate to near dryness, redissolve in water, and test with silver nitrate. Both give sign of reconversion into common phosphate by the production of a yellow precipitate.

Sodium Arsenates.—These salts closely resemble the corresponding phosphates. On adding sodium carbonate to a solution of arsenic acid till an alkaline reaction becomes apparent, and evaporating, the salt $Na_2HAsO_4,12H_2O$ is produced, indistinguishable in appearance from common sodium phosphate. This salt also crystallises with $7H_2O$. It is usually prepared by melting in a crucible an intimate mixture of white arsenic (10 parts), sodium nitrate ($8\frac{1}{2}$ parts), and trisodium carbonates ($5\frac{1}{2}$ parts), then redissolving the mass in water and crystallising.—The *trisodium salt*, $Na_3AsO_4,12H_2O$, is formed when sodium carbonate in excess is fused with arsenic acid, or when the preceding salt is mixed with caustic soda.—The *monosodium salt*, NaH_2AsO_4,H_2O, is made by substituting an excess of arsenic acid for the solution of alkali. The alkaline arsenates which contain basic water lose the latter at a red heat, but, unlike the phosphates, recover it when again dissolved. The arsenates of the alkalis are soluble in water: those of the earths and other metallic oxides are insoluble, but are dissolved by acids. The reddish-brown precipitate with silver nitrate is highly characteristic of arsenic acid.

An impure sodium arsenate is largely used in calico printing as a substitute for cow-dung, in clearing cloth after mordanting: it is known in the trade as "dung substitute."

Sodium Borates.—The *Orthoborate*, Na_3BO_3, is obtained by fusing boron trioxide with excess of caustic soda, according to the equation: $B_2O_3 + 6NaOH = 2Na_3BO_3 + 3H_2O$. It is very unstable, being resolved by solution in water into a hydrated metaborate and sodium hydroxide: $Na_3BO_3 + H_2O = NaBO_2 + 2NaOH$.

The *Pyroborate*, or *Borax*, $Na_2B_4O_7$, $10H_2O$ or $Na_2O,2B_2O_3,10H_2O$, occurs in the waters of certain lakes in Thibet and Persia, and is imported in a crude state from India under the name of *tincal*. When purified it constitutes the borax of commerce. Much borax is now, however, manufactured from the native boric acid of Tuscany, also from a native calcium borate called *hayesine*, which occurs in Southern Peru. Large quantities of borax are also obtained from the borax lake in California, the water of which contains a pound of crystallised borax in 13 gallons. Borax crystallises in six-sided prisms, which effloresce in dry air, and require 20 parts of

cold and 6 of boiling water for solution. On exposing it to heat, the 10 molecules of water of crystallisation are expelled, and at a higher temperature the salt fuses, and assumes a glassy appearance on cooling: in this state it is much used for blow-pipe experiments, the metallic oxides dissolving in it to transparent beads, many of which are distinguished by characteristic colours. By particular management, crystals of borax can be obtained with 5 molecules of water: they are very hard, and permanent in the air. Borax, though by constitution an acid salt, has an alkaline reaction to test-paper. It is used in the arts for soldering metals, its action consisting in rendering the surfaces to be joined metallic, by dissolving the oxides; and it sometimes enters into the composition of the glaze with which stoneware is covered.—*Octahedral Borax*, $Na_2B_4O_7,5H_2O$, is deposited when a supersaturated solution of borax is allowed to evaporate in a warm place.

Sodium Metaborate, $NaBO_2$ or Na_2O,B_2O_3, is obtained by fusing common borax and sodium carbonate together in equivalent proportions, and dissolving the mass in water. It forms large monoclinic crystals, having the composition $NaBO_2,3H_2O$.

Experiments with borax.—1. Melt borax upon a loop of platinum wire by making the wire red-hot, dipping it into the powdered salt, and then holding the mass in the Bunsen flame. Observe that the bead is clear and colourless. Now apply to it a drop of solution of cobalt nitrate, and heat it again. A blue glass results. In the same way prepare beads, and colour them by means of compounds of copper, iron, and chromium.

2. Dissolve about 10 grams of borax in ten times as much boiling water, add to the liquid enough hydrochloric acid to render it strongly acid, and allow it to cool. Crystals of boric acid, H_3BO_3, are deposited. Filter off the crystals when cold, drain them, dissolve a portion in a little spirit of wine. Place the solution in a dish, set fire to it, and observe the green colour of the flame.

Sodium Silicates.—The *Metasilicate*, Na_2SiO_3, or Na_2O,SiO_2, obtained by fusing silica and sodium carbonate together in molecular proportions, is soluble in water and separates on evaporation in crystals containing $7H_2O$. With excess of sodium carbonate, the $\frac{4}{3}$-*silicate* $Na_8Si_3O_{10}$ or $4Na_2O,3SiO_2$, is obtained, as shown by the equation $3SiO_2+4(Na_2O,CO_2)=4Na_2O,3SiO_2+4CO_2$.

The *Quadrisilicate*, $Na_2Si_4O_9$ or $Na_2O,4SiO_2$, commonly known as silicate of soda or *soluble glass*, is prepared by heating white sand (180 parts), soda-ash (100 parts), and charcoal (3 parts), in a reverberatory furnace, or by dissolving powdered flint under pressure in a hot concentrated solution of caustic soda. The first method yields it in the form of a transparent glassy mass, generally having a yellow, brown, or green colour, and dissolving readily, when pulverised, in boiling water, to a thick viscid liquid. It is used in the manufacture of artificial stone, which is made by mixing the soluble glass with sand and lime; also as a cement for joining

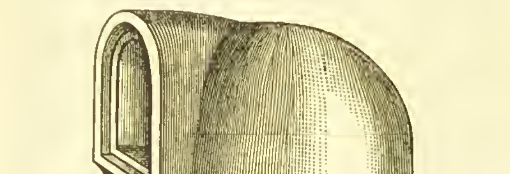
broken surfaces of porcelain, stone, etc. ; in fixing fresco colours by the process of stereochromy, and for the manufacture of silicated soap, which is prepared in large quantities by adding a solution of sodium silicate to the soap while setting.

Manufacture of Glass.—Ordinary glass is a mixture of various insoluble silicates with excess of silica, altogether destitute of crystalline structure : the simple silicates, formed by fusing the bases with silicic acid in equivalent proportions, very often crystallise, which happens also with the greater number of the natural silicates included among the earthy minerals. Compounds identical with some of these are also occasionally formed in artificial processes, where large masses of melted glassy matter are suffered to cool slowly. The alkaline silicates, when in the fused state, have the power of dissolving a large quantity of silica.

Two principal varieties of glass are met with in commerce, namely, glass composed of silica, alkali, and lime ; and glass containing a large proportion of lead silicate ; *crown* and *plate glass* belong to the former division ; *flint glass* and the material of artificial gems, to the latter. The lead promotes fusibility, and confers also density and lustre. Common green bottle-glass contains no lead, but much silicate of iron, derived from the impure materials.

The principle of the glass manufacture is very simple. Silica, in the shape of sand, is heated with potassium or sodium carbonate, and slaked lime or lead oxide : at a high temperature, fusion and combination occur, and carbon dioxide is expelled. Sodium sulphate (salt-cake) mixed with charcoal is often substituted for soda. When the melted mass has become perfectly clear and free from air-bubbles, it is left to cool until it assumes the peculiar tenacious condition proper for working.

Fig. 124.



The operation of fusion is conducted in large crucibles of refractory fire-clay, which in the case of lead-glass are covered by a dome at the top (see fig. 124), and have an opening at the side, by which the materials are introduced, and the melted glass withdrawn. Great care is exercised in the choice of the sand, which must be quite white and free from iron oxide. Red lead, one of the higher oxides, is preferred to litharge, although immediately reduced to monoxide by the heat, the liberated oxygen serving to destroy any combustible matter

that might accidentally find its way into the crucible, and stain the glass by reducing a portion of the lead. Potass gives a better glass than soda, although the latter is very generally employed, from its lower price. A certain proportion of broken and waste glass of the same kind is always added to the other materials.

Articles of blown glass are thus made : The workman begins by collecting a proper quantity of soft pasty glass at the end of his *blow-pipe*, an iron tube 5 or 6 feet in length, terminated by a mouth-piece of wood; he then begins blowing, by which the lump is expanded into a kind of flask, susceptible of having its form modified by the position in which it is held, and the velocity of rotation continually given to the iron tube. If an open-mouthed vessel is to be made, an iron rod, called a *pontil* or *puntil*, is dipped into the glass-pot, and applied to the bottom of the flask, to which it thus serves as a handle, the blow-pipe being removed by the application of a cold iron to the neck. The vessel is then reheated at a hole left for the purpose in the wall of the furnace, the aperture is enlarged, and the vessel otherwise altered in figure by the aid of a few simple tools, until completed. It is then detached, and carried to the annealing oven, where it undergoes slow and gradual cooling during many hours, the object of which is to obviate the excessive brittleness always exhibited by glass which has been quickly cooled. The large circular *tables* of crown glass are made by a very curious process of this kind ; the globular flask at first produced, transferred from the blow-pipe to the pontil, is suddenly made to assume the form of a flat disc by the centrifugal force of the rapid rotatory movement given to the rod. *Plate glass* is cast upon a flat metal table, and after very careful annealing is ground true and polished by suitable machinery. Tubes are made by rapidly drawing out a hollow cylinder ; and from these a great variety of useful small apparatus may be constructed with the help of a lamp and blow-pipe, worked by bellows. Small tubes may be bent in the flame of a spirit-lamp or gas-jet, and cut with a file, a scratch being made, and the two portions pulled or broken asunder in a way easily learned by a few trials.

Specimens of the two chief varieties of glass gave on analysis the following results :—

Bohemian plate glass (excellent).		English flint glass.	
Silica,	60·0	Silica,	51·93
Potassium oxide,	25·0	Potassium oxide,	13·77
Lime,	12·5	Lead oxide,	33·28
	97·5		98·98

The difficultly fusible white Bohemian tube, so valuable in organic analysis, has been found to contain, in 100 parts—

Silica,	72·80
Lime, with traces of alumina,	9·68
Magnesia,	·40
Potassium oxide,	6·80
Traces of manganese, etc., and loss,	·32

Different colours are often communicated to glass by metallic oxides. Thus, oxide of cobalt gives deep blue ; oxide of manganese, amethyst ; cuprous oxide, ruby-red ; cupric oxide, green ; the oxides of iron, dull green or brown, etc. These oxides are either added to the melted contents of the glass-pot, in which they dissolve, or applied in a particular manner to the surface of the plate or other object, which is then reheated, until fusion of the colouring matter occurs ; such is the practice of enamelling and glass-painting. An opaque white appearance is given by oxide of tin; the enamel of watch-faces is thus prepared.

Toughened Glass.—When ordinary glass is heated till it begins to soften, then plunged into melted paraffin, wax, or other substance melting at a comparatively low temperature, and left to cool gradually, it becomes very tough, so that it may be struck or thrown on the ground without breaking. It has also acquired greater power of resisting sudden changes of temperature, and may be heated to redness, then dipped into cold water, and whilst wet again held in the flame, without injury. Hence it is well adapted for lamp-chimneys and for culinary vessels. When it does break, however, it splits up into a multitude of minute angular fragments.

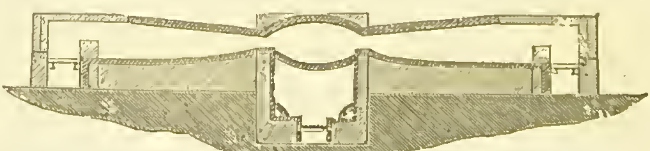
Sodium Carbonates. — The *Normal* or *Disodic Carbonate*, $Na_2CO_3,10H_2O$, was once exclusively obtained from the ashes of sea-weeds, and of plants, such as the *Salsola Soda*, which grow by the sea-side, or, being cultivated in suitable localities for the purpose, are afterwards subjected to incineration. The *barilla*, which is no longer of any commercial importance, was thus produced in several places on the coast of Spain, as at Alicante, and Carthagena. That made in Brittany was called *varec*.

Sodium carbonate is now manufactured on a stupendous scale from common salt by a series of processes, of which one invented by Nicolas Leblanc has now been employed for about a century.

Leblanc's process may be considered as divisible into two stages :—(1) Manufacture of sodium sulphate, or salt-cake, from sodium chloride (common salt) ; this is called the salt-cake process. (2) Manufacture of sodium carbonate, or soda-ash ; called the soda-ash process.

1. *Salt-Cake Process.*—This process consists in the decomposition of common salt by sulphuric acid, and is effected in a furnace called the *salt-cake furnace*, of which fig. 125 represents a section.

Fig. 125.



It consists of a large covered iron pan, placed in the centre, and heated by a fire underneath ; and two roasters, or reverberatory

furnaces, placed on either side, and on the hearths of which the salt is completely decomposed. The charge of half a ton of salt is first placed in the iron pan, and then the requisite quantity of sulphuric acid is allowed to pass in upon it. Hydrochloric acid is evolved, and escapes through a flue, with the products of combustion, into towers or scrubbers, filled with coke and bricks moistened with a stream of water ; the acid vapours are thus condensed, and the smoke and heated air pass up the chimney. After the mixture of salt and acid has been heated in the iron pan, it becomes converted into a solid mass of acid sodium sulphate and undecomposed sodium chloride :—

$$2NaCl + H_2SO_4 = NaCl + NaHSO_4 + HCl.$$

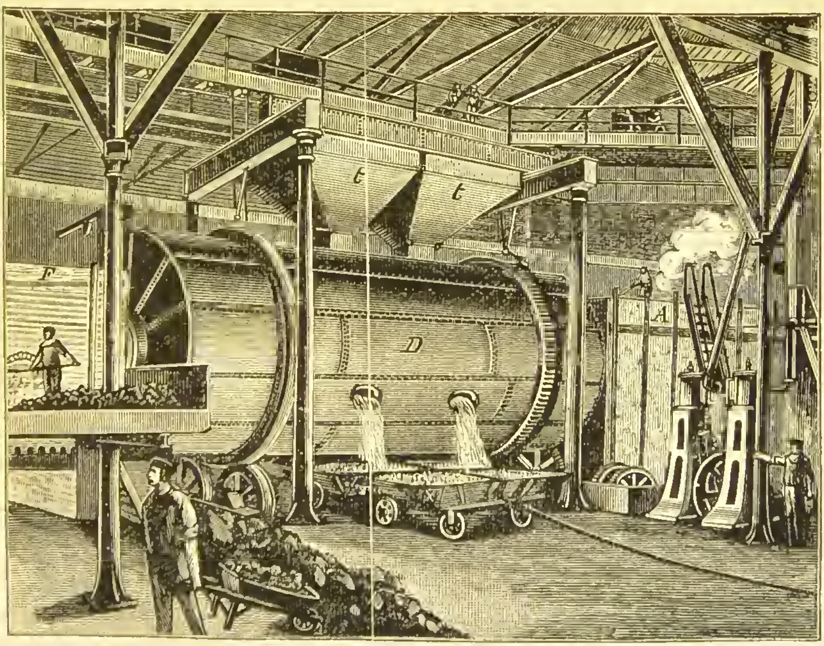
It is then raked on to the hearth of one of the furnaces at the side of the decomposing pan, where the flame and heated air of the fire complete the decomposition into neutral sodium sulphate and hydrochloric acid:—

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl.$$

The roasters are employed alternately.

2. *Soda-Ash Process.*—The sulphate is next mixed with an equal

Fig. 126.



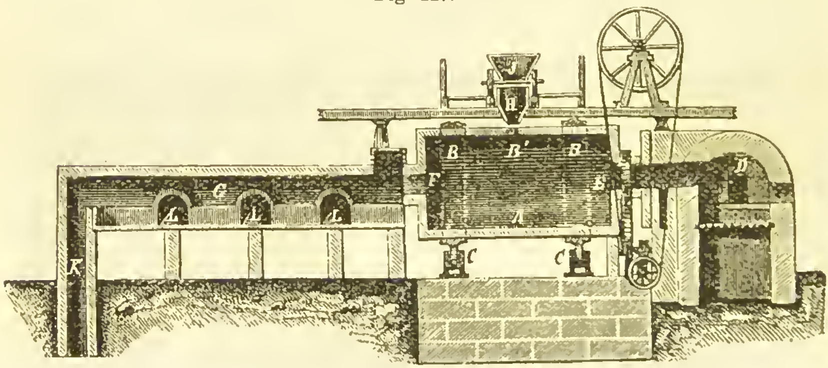
weight of chalk or limestone, and half as much small coal, both ground or crushed. The mixture is thrown into a reverberatory

furnace, and heated to fusion, with constant stirring. When the decomposition is judged complete, the melted matter is raked from the furnace into an iron trough, where it is allowed to cool.

In many works the black ash is made in a furnace of a different kind, designed to effect a saving of hand labour. A large cylindrical drum lined with firebrick is supported in such a manner that, actuated by a small steam-engine, it can be made to rotate horizontally upon its long axis. This "revolver" (fig. 126), as it is called, has an aperture at each end by which the hot gases from a furnace adjoining (shown at F in the figure) can be made to pass centrally through it, and so to heat the materials which are placed inside. The waste heat passes off at the opposite end and is utilised for evaporating the liquors afterwards obtained.

The materials are charged into the furnace through a hopper, into which they are delivered from trucks which approach by means of an overhead tram-line. When each charge has been sufficiently heated, the rotation of the revolver is stopped, and the aperture in its side brought over the small iron trucks which are placed below for the reception of the product.

Fig. 127.

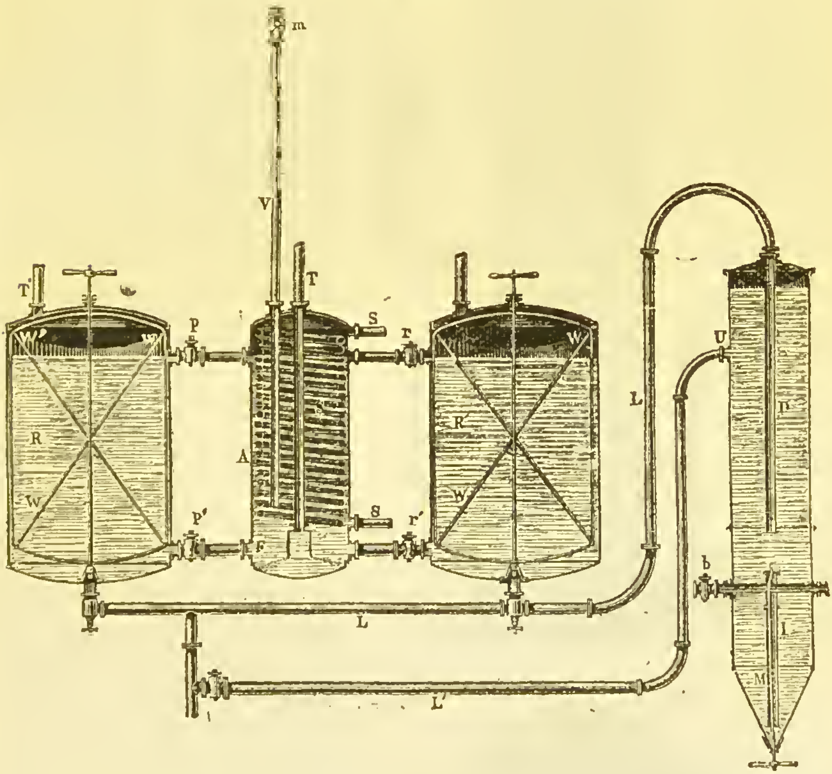


The relative positions of the several parts of the apparatus are shown more clearly in the section given in fig. 127, where A B is the revolver, D the furnace, E the entrance of the hot gases from the fire, F the aperture by which they pass from the revolver to the space above the liquid contained in the pans G, while at L are shown the arches in the side wall of the evaporating pan by which the salts are withdrawn from the boiling liquor.

The crude product of these operations, called *black ash* or *ball-soda*, is broken up into little pieces, when cold, and lixiviated with cold or tepid water. The solution is boiled down rapidly in the pans above mentioned, and when sufficiently concentrated it deposits small crystals of sodium carbonate containing one molecule of water, $Na_2CO_3H_2O$, and known as "soda salts." These crystals are fished out by means of perforated ladles while the liquid is hot, as they

would redissolve in the form of a hydrate richer in water if allowed to cool in the solution. The soda salts, mixed with a little sawdust, are calcined in a suitable furnace, and produce the best "soda ash,' which contains about 96 per cent. of sodium carbonate, Na_2CO_3, with very small quantities of chloride and sulphate. The liquors from which the salts have been deposited contain a considerable quantity of sodium hydroxide, and are usually boiled with lime and evaporated down for the production of caustic soda. By dissolving soda-ash in hot water, filtering the solution, and then allowing it to cool slowly the carbonate is deposited in large transparent crystals.

Fig. 128.



The reaction which takes place in the calcination of the sulphate with limestone and coal-dust seems to consist, first, in the conversion of the sodium sulphate into sulphide by the aid of the combustible matter, and, secondly, in the interchange of elements between that substance and the calcium carbonate :—

$$Na_2S + CaCO_3 = CaS + Na_2CO_3 .$$

A portion of the limestone is converted into lime by the heat, and consequently when the mass is treated with water, this reacts upon

the sodium carbonate, or produces a certain amount of hydroxide, which is now usually turned to account as above described.

Fig. 129.

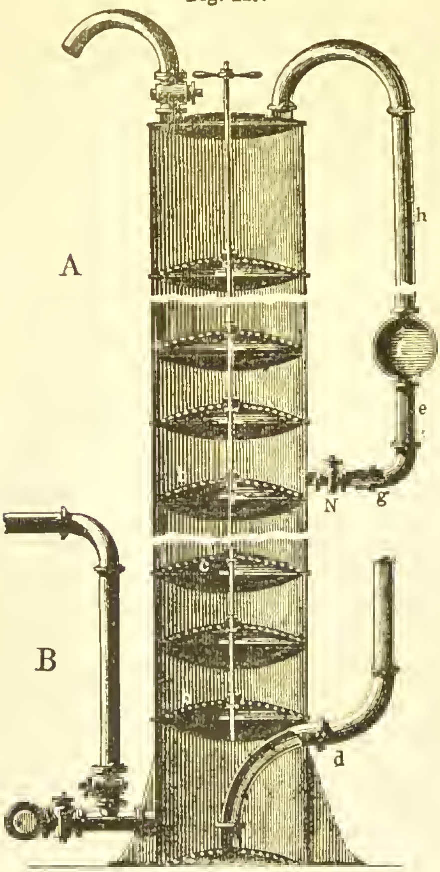
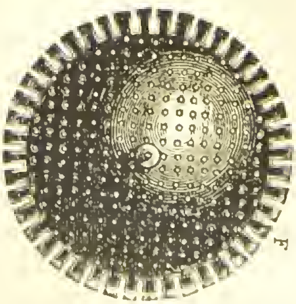


Fig. 130.



In the Leblanc process a serious difficulty has always arisen from the accumulation in and about the works of the insoluble part of the black-ash. This residue, the "soda-waste" of the alkali-maker, consisting largely of calcium sulphide, carries off in a useless form the whole of the sulphur of the sulphuric acid employed in the process. Many attempts have been made to recover the sulphur from the waste. One of these has already been described (p. 118).

Ammonia-soda Process.—Several other processes for the manufacture of soda have been proposed, but the only one which has attained commercial success is that above named, which was first suggested about forty years ago, and is now largely employed in England, on the Continent of Europe, and in the United States. It consists in decomposing a solution of common salt mixed with ammonia by means of carbonic acid under slight pressure. The apparatus in which the brine is first saturated with ammonia is shown in figure 128, in which r and r' are two vessels holding the brine, each provided with an agitator and communicating at the top and bottom with the tank A into which ammonia gas, together with a little carbon dioxide, is admitted by the pipe T. The solution of natural salt is always contaminated with magnesium chloride and calcium sulphate, and to precipitate the magnesium a little slaked

lime is added to the liquid. A precipitate is therefore formed consisting of magnesium and calcium carbonates, which is removed by subsidence, partly in the vessels r r' which are used alternately, partly in the continuous settling cylinder D.

The clear ammoniacal brine is then introduced into tall cylindrical iron vessels, divided by some twenty horizontal partitions, as shown in figs. 129, 130, carbon dioxide gas being pumped in at the bottom. The reaction which ensues results in the production of sodium bi-carbonate which, in consequence of its comparatively slight solubility, is precipitated as a crystalline powder while ammonium chloride remains in solution.

$$NaCl + NH_3 + H_2O + CO_2 = NaHCO_3 + NH_4Cl.$$

The carbon dioxide required in the operation is drawn from a lime kiln which yields an equivalent quantity of lime. The sodium bicarbonate is collected, dried and heated in ovens where it is converted into the normal carbonate, half the carbon dioxide being again evolved, so that it can be utilised:—

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

Hence the quantity of lime made is just sufficient for regenerating from the ammonium chloride the ammonia required in a subsequent operation. The chief advantages of this process are the direct conversion of the sodium chloride into carbonate, which is precipitated from the concentrated liquors uncontaminated with salts of other metals; the absolute freedom of the product from sulphur-compounds; and, lastly, simplicity of plant, saving of fuel, and freedom from noxious vapours and troublesome secondary products.

Its employment on the large scale was, however, for some time retarded by a loss of ammonia which was found very difficult to obviate; but this loss has by recent improvements been to a great extent overcome, and the ammonia-process is now rapidly gaining ground on that of Leblanc. The following table, drawn up from the annual reports of the Chief Inspector under the Alkali-works Regulation Act, shows that the quantity of soda made by the ammonia-process has been steadily increasing.

Tons of Salt Decomposed for the Production of Soda.

Year, ...	1886	1890	1891	1892	1893	1894	1895
Leblanc, . . .	649,248	602,769	567,863	519,593	467,562	434,298	408,173
Ammonia-Soda, . .	137,220	252,260	278,528	304,897	349,609	361,603	428,614
	786,468	855,029	846,391	824,490	817,171	795,901	836,787

From various causes, indeed, which cannot here be discussed, the Leblanc process, so far as the production of soda itself is concerned, has ceased to yield any profit, and the hydrochloric acid which is evolved in the salt-cake process yields only a small profit; so that the process is now carried on mainly for the sake of certain secondary products which are obtained by it. The sulphuric acid used for decomposing the sodium chloride is made almost exclusively from the sulphur of pyrites, and the pyrites used for the purpose in this country is either Spanish or Portuguese pyrites, both of which contain from 3 to 4 per cent. of copper, together with very small quantities of silver and gold; and after the greater part of the sulphur has been burnt off, these metals, together with iron oxide, remain in the "burnt ore" or "pyrites cinders," as the residue is called, which is then treated by a wet process for the extraction of the copper (see *Copper*), and the residue then left is an almost pure oxide of iron, which can be used for various purposes in the manufacture of iron and steel. It is to these secondary products that the profits still obtained by the Leblanc process are due.

Experiments.—1. Take a large crystal of soda, rinse it with water, and wipe it dry with filter paper. The surface should be bright and smooth; place the crystal in a small dish, and weigh the whole; now leave it exposed to the air of a warm room for a day or two. The crystal soon becomes opaque, and ultimately crumbles to a powder, at the same time losing weight from loss of water. This change is called "efflorescence."

2. Place a little dry carbonate of potassium in a small dish, and weigh the whole: then leave it exposed to air for a day, and weigh again. There will be considerable increase of weight, and the salt will be observed to have become damp, or even to have liquefied, according to the state of the weather. This change owing to absorption of moisture is called "deliquescence."

Properties of Normal Sodium Carbonate.—The ordinary crystals of sodium carbonate contain 10 molecules of water (washing soda); but by crystallisation from a warm solution the same salt may be obtained with 7 molecules, or from a boiling solution with only one. The ordinary crystals are monoclinic; they effloresce in dry air, and crumble to a white powder. Heated, they fuse in their water of crystallisation: when the latter has been expelled and the dry salt exposed to a full red heat, it melts without undergoing change. The common crystals dissolve in 2 parts of cold, and in less than their own weight of boiling water: the solution has a strong, disagreeable, alkaline taste, and a powerfully alkaline reaction.

Hydrogen and Sodium Carbonate, Hydrosodic. Carbonate, Monosodic Carbonate, $NaHCO_3$ or Na_2CO_3,H_2CO_3, commonly called *Bicarbonate of Soda.*—This salt is prepared by passing carbonic acid gas into a cold solution of the normal carbonate, or by placing the crystals in an atmosphere of the gas, which is rapidly absorbed, while the crystals lose the greater part of their water, and pass into the new compound.

Monosodic carbonate, prepared by either process, is a crystalline white powder, which cannot be redissolved in warm water without partial decomposition. It requires 10 parts of water at 15·5° for solution : the liquid is feebly alkaline to test-paper, and has a much milder taste than that of the normal carbonate. It does not precipitate a solution of magnesium sulphate. By exposure to heat, the salt is converted into normal carbonate.

Dihydro-tetrasodic Carbonate, $Na_4H_2(CO_3)_3,2H_2O$.—This salt, commonly called *Sesquicarbonate of Soda*, may be regarded as a compound of the normal and hydric salts ($Na_2CO_3,2NaHCO_3$). It occurs native on the banks of the soda lakes of Sokenna, near Fezzan, in Africa, where it is called *trona* ; also as *urao*, at the bottom of a lake in Maracaibo, South America. It is now produced artificially by mixing the monosodium and disodium carbonates in the proportions above indicated, and crystallising the solution at slightly elevated temperature.

Sodium and *Potassium Carbonate*, $NaKCO_3,6H_2O$, separates in monoclinic crystals from a solution containing the two carbonates in equivalent proportions.

A mixture of these two carbonates in equivalent proportions melts at a much lower temperature than either of the salts separately ; a mixture of the dry salts is used under the name of *fusion-mixture* in the analysis of silicates, etc.

Sodium Sulphide, Na_2S, is prepared like potassium sulphide, and separates from a concentrated solution in octahedral crystals, which are rapidly decomposed by contact with the air, yielding a mixture of hydroxide and thiosulphate of sodium. It forms soluble sulphur-salts with hydrogen sulphide, carbon bisulphide, and other electro-negative sulphides.

There is no good precipitant for sodium, all its salts being somewhat freely soluble in water. The pyroantimonate is precipitated on mixing a solution of a sodium salt with a solution of potassium pyroantimonate ; the use of this reagent is, however, attended with some difficulties. The oxalate $Na_2C_2O_4$ is also distinguished by its slight solubility. The yellow colour imparted by sodium salts to the blow-pipe or Bunsen flame is a character of considerable importance. The spectral reactions of sodium compounds have been already noticed (p. 333 and coloured plate). As sodium compounds are widely diffused in small quantity in the dust of the atmosphere, in water, and in many metallic salts, the production of a temporary yellow light in the flame cannot be regarded as sufficient evidence of the presence of sodium as the chief constituent in a salt under examination. In such cases the question may be decided by converting the salt into sulphate, which can be recognised by its crystalline form, quite distinct from that of potassium sulphate, and by its peculiarities of solubility. The crystalline form of the chloride, common salt, is also very distinctive.

LITHIUM.

Symbol, Li. Atomic weight, 7.

Lithium is found in petalite, spodumene, lepidolite, triphylline, and a few other minerals, and sometimes occurs in minute quantities in mineral springs. The most abundant source of it yet discovered is the mineral water of Wheal Clifford in Cornwall, in which it exists to the amount of 61 parts in a million.

A lithium salt may be obtained from petalite by the following process. The mineral is reduced to a fine powder, mixed with 5 or 6 times its weight of pure calcium carbonate, with a little sal-ammoniac, and the mixture is heated strongly in a platinum crucible for an hour. The shrunken coherent mass is digested in dilute hydrochloric acid, the whole evaporated to dryness, acidulated water added, and the silica separated by a filter. The solution is then mixed with ammonium carbonate in excess, boiled and filtered; the clear liquid is evaporated to dryness and gently heated in a platinum crucible to expel the sal-ammoniac; and the residue is wetted with oil of vitriol, gently evaporated once more to dryness, and ignited: pure fused lithium sulphate then remains.

The metal is obtained by fusing pure lithium chloride in a small thick porcelain crucible, and decomposing the fused chloride by electrolysis. It is a white metal like sodium, and very oxidisable. Lithium melts at 180°; its density is 0·59: it is, therefore, the lightest solid known.

Lithium hydroxide, or *Lithia*, LiHO, is much less soluble in water than the hydroxides of potassium and sodium; the *carbonate* and *phosphate* are also sparingly soluble salts. The *chloride* crystallises in anhydrous cubes which are deliquescent. *Lithium sulphate* is a very beautiful salt, crystallising in lengthened prisms which contain 1 molecule of water. It gives no crystallisable double salt with aluminium sulphate, probably on account of its great solubility.

The salts of lithium colour the outer flame of the blow-pipe carmine-red. The spectral phenomena exhibited by lithium compounds are mentioned on page 333. *See* also the coloured plate.

CÆSIUM AND RUBIDIUM.

Ca = 133. Rb = 85·4.

The two metals designated by these names were discovered by Bunsen by means of the method of spectrum analysis: the former in 1860 and the latter in 1861. These metals, it appears, are widely diffused in nature, but always occur in very small quantities: they have been detected in many mineral waters, as well as in some minerals, namely, lithia-mica or lepidolite, in petalite, and in felspar;

they have also been found in the alkaline ashes of beetroot. The salt-spring of Dürckheim contains 0·17 part of cæsium chloride in a million parts of water, but it appears that the hot spring of Wheal Clifford, already mentioned as a source of lithium, contains 1·71 parts of cæsium chloride in a million, or 0·12 grain in a gallon.

The best material for the preparation of rubidium is lepidolite, which has been found to contain as much as 0·2 per cent. of that metal. Both metals are closely allied to potassium in their deportment.

Rubidium and cæsium, like potassium, form double salts with tetrachloride of platinum, which are, however, much less soluble than the corresponding potassium salts: it is on this property that the separation of these metals from potassium is based. The mixture of platinochlorides is repeatedly extracted with boiling water, when a difficultly soluble residue, consisting chiefly of the platinochlorides of cæsium and rubidium, remains; and these two metals are finally separated by converting them into tartrates, rubidium tartrate requiring for solution eight times as much water as cæsium tartrate, and therefore crystallising out first from the mixed solution. According to Cossa, the separation is best effected by treating a solution of cæsium and rubidium alums with antimony trichloride which throws down the whole of the cæsium, leaving the rubidium in solution.

The hydroxides of these metals are powerful alkalis which absorb carbon dioxide from the air, passing first into normal and then into bicarbonates. Cæsium carbonate is soluble in absolute alcohol; rubidium carbonate is nearly insoluble in that liquid: this property is made use of for the separation of these two metals. Cæsium chloride crystallises in cubes, and is somewhat more soluble in water than chloride of potassium.

Rubidium chloride, in a fused state, is easily decomposed by the electric current; the metal produced rises to the surface and burns with a reddish light. If this experiment be performed in an atmosphere of hydrogen, to prevent oxidation, the separated metal is nevertheless lost, dissolving in the fused chloride, which is transformed into a subchloride having the blue colour of smalt.

Rubidium, when separated under mercury by the electric current, forms a silvery crystalline amalgam, which oxidises rapidly on exposure to the air, and decomposes water at ordinary temperatures.

Metallic cæsium cannot readily be obtained, either by the electrolysis of its chloride, or by heating its acid tartrate with sugar, charcoal, and chalk, but it may be prepared by electrolysis of its cyanide, which is formed on passing anhydrous hydrocyanic acid into a solution of cæsium hydroxide in absolute alcohol. To prepare the metal, a mixture of barium cyanide (1 pt.) and cæsium cyanide (4 pts.) is fused in a porcelain crucible, and an electric current is passed through the molten mass, aluminium poles being used. On warming the contents of the crucible under petroleum, the metal separates into globules. Metallic cæsium is silver-white, like potas-

sium and rubidium, and soft at ordinary temperatures; sp. gr. 1·88 at 15°; melting-point, 26–27°. It oxidises quickly in the air, and takes fire when thrown on water.

AMMONIUM.

The ammonia salts are most conveniently studied in this place, on account of their close analogy to those of potassium and sodium. These salts are formed by the direct union of ammonia, NH_3, with acids, and as already pointed out (p. 149), they may be regarded as compounds of acid radicles, Cl, NO_3, SO_4, &c., with a basylous radicle, NH_4, called ammonium, which plays in these salts the same part as potassium and sodium in their respective compounds; thus:—

NH_3 Ammonia.	+	HCl Hydrochloric acid.	=	$NH_4.Cl$ Ammonium chloride.
NH_3	+	HNO_3 Nitric acid.	=	$NH_4.NO_3$ Ammonium nitrate.
NH_3	+	H_2SO_4 Sulphuric acid.	=	$NH_4.SO_4H.$ Acid ammonium sulphate.
$2NH_3$	+	H_2SO_4	=	$(NH_4)_2SO_4.$ Normal ammonium sulphate.

The radicle NH_4 is not capable of existing in the free state; it is simply the residue which is left on removing the atom of chlorine from the saturated molecule, NH_4Cl. Whether the double molecule N_2H_8, or $\begin{matrix} NH_4 \\ | \\ NH_4 \end{matrix}$, is capable of a separate existence, is a different question. Ammonium is said, indeed, to be capable of forming an amalgam with mercury; but even in this state it is quickly resolved into ammonia and free hydrogen.

When a globule of mercury is placed on a piece of moistened potassium hydroxide, and connected with the negative side of a voltaic battery, the circuit being completed through the platinum plate upon which the alkali rests, decomposition of the latter takes place, and an amalgam of potassium is rapidly formed. If this experiment be now repeated with a piece of sal-ammoniac instead of potassium hydroxide, a soft, solid, metalline mass is also produced, which has been called *ammonium amalgam*, and considered to contain ammonium, NH_4, in combination with mercury. A simpler method of preparing this compound is to place a mass of sodium amalgam in a dish and cover it with a saturated solution of sal-ammoniac in cold water. The production of a spongy mass instantly commences,

the mercury increasing prodigiously in volume, and becoming quite pasty. The increase of weight is, however, quite trifling, varying from $\frac{1}{1800}$ to $\frac{1}{1200}$ part. Left to itself, the amalgam quickly decomposes into fluid mercury, ammonia, and hydrogen. It is probable, indeed, that the so-called amalgam may be nothing more than mercury which has absorbed a certain quantity of these gases ; just as silver, when heated to a very high temperature, is capable of taking up about twenty times its volume of oxygen gas, which it gives up again on cooling.

But whether ammonium has any separate existence or not, it is quite certain that many ammoniacal salts are isomorphous with those of potassium ; and if from any two of the corresponding salts, as the nitrates KNO_3 and NH_4NO_3, we subtract the radicle NO_3 common to the two, there remain the atom K and the group NH_4, which are, therefore, supposed to be isomorphous.

Ammonium Chloride, Sal-Ammoniac, NH_4Cl or NH_3,HCl.—Sal-ammoniac was formerly obtained from Egypt, being extracted by sublimation from the soot of camels' dung : it is now manufactured from the ammoniacal liquid of the gas-works, and from the similar liquid obtained from various forms of coke-oven, and in a few places from the gases of the blast-furnace ; it is also obtained from the condensed products of the distillation of bones and other animal refuse, in the preparation of animal charcoal.

These impure and highly offensive solutions are treated with a slight excess of lime, by which the carbonate, sulphide, and other salts are decomposed and ammonia evolved in the gaseous state. This is passed into the acid contained in a separate vessel, and the salt, which ultimately crystallises from the liquid, is drained and then purified by sublimation in large iron vessels lined with clay, surmounted with domes of lead. Sublimed sal-ammoniac has a fibrous texture, and is tough and difficult to powder.

Sal-ammoniac separates from its aqueous solution in radiate groups of small but distinct cubes and octahedrons. It has a sharp saline taste, and dissolves in $2\frac{3}{4}$ parts of cold, and in a much smaller quantity of hot water. By heat, it is sublimed without decomposition. The crystals are anhydrous. Ammonium chloride forms double salts with the chlorides of magnesium, nickel, cobalt, manganese, zinc, copper, and other metals.

Experiments.—1. Mix 20 to 30 cubic centimetres of strong hydrochloric acid with an equal quantity of water, and add solution of ammonia, with continual stirring, till a drop of the liquid placed on red litmus paper turns it blue. Evaporate the solution to half its bulk, and let it cool. If crystals are not formed, evaporate further and cool again. Observe the form of the crystals.

2. Place about a gram of dry sal-ammoniac at the bottom of a dry test-tube, and apply heat. The salt sublimes without melting, and condenses as a white sublimate upon the upper cool part of the tube. No residue should be left.

Ammonium Sulphate, $(NH_4)_2SO_4$.—Prepared by neutralising ammonium carbonate with sulphuric acid, or on the large scale, for use as a manure, by passing ammonia, evolved by heating gas-liquor with lime, into sulphuric acid and crystallising. It is soluble in 2 parts of cold water, and crystallises in long, flattened, six-sided prisms. It is entirely decomposed and driven off by ignition, and, even to a certain extent, by long boiling with water, ammonia being expelled and the liquid rendered acid.

Ammonium Nitrate, $(NH_4)NO_3$, is easily prepared by adding ammonium carbonate to slightly diluted nitric acid until neutralisation has been reached. By slow evaporation at a moderate temperature it crystallises in six-sided prisms, like those of potassium nitrate; but, as usually prepared for making nitrogen monoxide, by quick boiling until a portion solidifies completely on cooling, it forms a fibrous and indistinctly crystalline mass.

Ammonium nitrate dissolves in 2 parts of cold water, producing considerable depression of temperature; it is but slightly deliquescent, and deflagrates like nitre on contact with heated combustible matter. Its decomposition by heat has been already explained (p. 161).

Ammonium Phosphates.—The *Normal* or *Triammonium Salt*, $(NH_4)_3PO_4$, is obtained as a crystalline mass when the diammonic salt is supersaturated with strong aqueous ammonia, and crystallises from dilute ammonia in short prismatic needles containing 3 molecules of water. This salt decomposes when its aqueous solution is boiled, giving off two-thirds of its ammonia.—The *diammonium salt*, $(NH_4)_2HPO_4$, occurs in guano from Ichaboe, and is deposited in transparent monoclinic prisms, when an aqueous solution of phosphoric acid containing excess of ammonia is left to evaporate.—The *monoammonium salt*, $(NH_4)H_2PO_4$, formed when aqueous phosphoric acid is added to aqueous ammonia till the solution becomes acid and is no longer precipitated by barium chloride, crystallises in quadratic prisms, isomorphous with the corresponding potassium salt.

Sodium, Ammonium, and Hydrogen Phosphate; Phosphorus Salt; Microcosmic Salt, $Na(NH_4)HPO_4,4H_2O$.—Six parts of common sodium phosphate are heated with 2 parts of water, until the whole is liquefied, and 1 part of powdered sal-ammoniac is added; common salt then separates, and may be removed by a filter; and from the solution, duly concentrated, the microcosmic salt is deposited in prismatic crystals, which may be purified by one or two recrystallisations. Microcosmic salt is very soluble. When gently heated, it parts with its 4 molecules of crystallisation-water, and, at a higher temperature, the basic hydrogen is likewise expelled as water, together with ammonia, and a very fusible compound, sodium metaphosphate, remains, which is valuable as a flux in blow-pipe experiments. Microcosmic salt occurs in decomposed urine.

Ammonium Carbonates.—There are three definite carbonates of ammonia, the composition of which is as follows:—

Normal or Diammonium carbonate,	$(NH_4)_2CO_3,H_2O$
Ammonium-hydrogen carbonate,	$(NH_4)HCO_3$
Sesqui-carbonate,	$(NH_4)_4H_2(CO_3)_3,H_2O$.

1. The *normal carbonate* is prepared by addition of ammonia to one of the acid salts, or of water to the carbamate of ammonia, $CO_2N_2H_6$ (p. 377), with certain special precautions, the description of which is too long for insertion in this work, to prevent the escape of a portion of the ammonia. It crystallises in elongated plates or flattened prisms, having a caustic taste, a powerful ammoniacal odour, and easily giving off ammonia and water, whereby they are converted into the acid carbonate :—

$$(NH_4)_2CO_3,H_2O = NH_3 + H_2O + (NH_4)HCO_3.$$

2. *Ammonium and Hydrogen Carbonate*, or *Monoammonic Carbonate*, $(NH_4)HCO_3$, commonly called *Bicarbonate of Ammonia*.—This salt is obtained by saturating an aqueous solution of ammonia, or of the half-acid carbonate, with carbonic acid gas ; or by treating the finely pounded half-acid carbonate with strong alcohol, which dissolves out normal or diammonium carbonate, leaving a residue of the monoammonium salt. Cold water may be used instead of alcohol for this purpose ; but it dissolves a large quantity of the monoammonium carbonate. All ammonium carbonates when left to themselves are gradually converted into monoammonium carbonate. This salt forms large crystals belonging to the trimetric system. According to Deville it is dimorphous, but never isomorphous with monopotassium carbonate ; when exposed to the air, it volatilises slowly, and gives off a faint ammoniacal odour. It dissolves in 8 parts of cold water, the solution decomposing gradually at ordinary temperatures, quickly when heated above 30°, with evolution of ammonia. It is insoluble in alcohol, but when exposed to the air, under alcohol, it dissolves as normal carbonate, evolving carbon dioxide.

It has been found native in considerable quantity in the deposits of guano on the western coast of Patagonia, in white crystalline masses, having a strong ammoniacal odour.

3. *Tetrammonio-dihydric Carbonate*, $N_4H_{18}C_3O_9 = (NH_4)_4H_2(CO_3)_3$. —This salt, commonly called *Sesquicarbonate of Ammonia*, contains the elements of 1 molecule of diammonium and 2 molecules of monoammonium carbonate, into which it is, in fact, resolved by treatment with water or alcohol :—

$$(NH_4)_4H_2(CO_3)_3 = (NH_4)_2CO_3 + 2(NH_4)HCO_3.$$

It is obtained by dissolving the commercial carbonate in strong aqueous ammonia, at about 30°, and crystallising the solution. It forms large transparent rectangular prisms, having their summits truncated by octahedral faces. These crystals decompose very rapidly in the air, giving off water and ammonia, and being converted into monoammonic carbonate.

Commercial carbonate of ammonia (*sal volatile, salt of hartshorn*)

consists of half-acid carbonate more or less mixed with carbamate. It is prepared on the large scale by heating a mixture of 1 part ammonium chloride or sulphate, and 2 parts calcium carbonate (chalk) in iron retorts or cylinders.

It is also made by mixing in lead chambers ammonia and carbon-dioxide gases in the presence of water.

Ammonium Sulphides.—Several of these compounds exist, and may be formed by distilling with sal-ammoniac the corresponding sulphides of potassium or sodium.

Ammonium and Hydrogen Sulphide, or *Ammonium Hydrosulphide*, $(NH_4)HS$, is obtained by saturating a solution of ammonia with well-washed sulphuretted hydrogen gas, until no more of the latter is absorbed. The solution is nearly colourless at first, but becomes yellow after a time if it has been exposed to the air. It gives precipitates with most metallic solutions, which are very often characteristic, and is of great service in analytical chemistry.

Experiment.—Fill an ordinary reagent bottle with common, 10 per cent., solution of ammonia, and pass into it a stream of washed H_2S gas, till on taking a small portion of the liquid in a test-tube, and adding to it solution of magnesium sulphate, no precipitate is visible. The liquid in the bottle may then be preserved for use.

Ammoniacal salts are easily recognised ; they are all decomposed or volatilised at a high temperature ; and when heated with calcium hydroxide or solution of alkaline carbonate, they give off ammonia, which may be recognised by its odour and alkaline reaction. The salts are all more or less soluble, the acid tartrate and the platino-chloride being, however, among the least soluble : hence ammonium salts cannot be distinguished from potassium salts by the tests of tartaric acid and platinum solution. When a solution containing an ammoniacal salt, or free ammonia, is mixed with potash, and a solution of *mercuric iodide* in *potassium iodide* is added, a brown precipitate or coloration is immediately produced, consisting of dimercurammonium iodide, $NHg_2I.H_2O$:—

$$NH_3 + 2HgI_2 = NHg_2I + 3HI.$$

This is called Nessler's test ; it is by far the most delicate test for ammonia that is known.

Amic Acids and Amides.

Sulphamic Acid.—When dry ammonia gas is passed over a thin layer of sulphuric oxide, SO_3, the gas is absorbed, and a white crystalline powder is formed, having the composition $N_2H_6SO_3$, that is, of ammonium sulphate minus one molecule of water :—

$$N_2H_6SO_3 = (NH_4)_2SO_4 - H_2O.$$

It is not, however, a salt of sulphuric acid; for its aqueous solution does not give any precipitate with baryta-water or soluble barium salts. It is, in fact, the ammonium salt of s u l p h a m i c a c i d, an acid derived from sulphuric acid, SO_4H_2 or $SO_2(HO)_2$, by substitution of the univalent radicle, NH_2 (p. 260), for one atom of hydroxyl, HO. The formula of this acid is $SO_2(NH_2)(OH)$, and that of its ammonium salt, $SO_2(NH_2)(ONH_4)$, or $SO_3N_2H_6$. Ammonium sulphamate is permanent in the air, and dissolves without decomposition in water. Its solution evaporated in a vacuum over oil of vitriol yields the salt in transparent colourless crystals.

The solution of the ammonium salt, mixed with baryta-water, gives off ammonia, and yields a solution of *barium sulphamate*, $[SO_2(NH_2)O]_2Ba$, which may be obtained by evaporation in well-defined crystals; and the solution of this salt, decomposed with potassium sulphate, yields *potassium sulphamate*, $SO_2(NH_2)(OK)$.

Carbamic Acid.—When dry ammonia gas is mixed with carbon dioxide, the mixture being kept cool, the gases combine in the proportion of 2 volumes of the former to 1 volume of the latter, forming a pungent, very volatile substance, which condenses in white flocks. This substance has the composition $CO_2N_2H_6$, that is, of normal ammonium carbonate, $CO_3(NH_4)_2$, *minus* one molecule of water. It exists, as already observed, in commercial carbonate of ammonia (p. 375). It was formerly called *anhydrous carbonate of ammonia*; but, like the preceding salt, it is not really a carbonate, but the ammonium salt of c a r b a m i c a c i d, $CO(NH_2)OH$, an acid derived from carbonic acid, CO_3H_2, or $CO(OH)_2$, by substitution of amidogen, NH_2, for one hydroxyl-group. Ammonium carbonate dissolves readily in water, and quickly takes up one molecule of that compound, whereby it is converted into normal ammonium carbonate.

Carbamide, CON_2H_4, or $CO(NH_2)_2$.—When ammonia gas is mixed with carbon oxychloride or phosgene gas, $COCl_2$, a white crystalline powder is formed, having this composition:—

$$COCl_2 + 2NH_3 = 2HCl + CON_2H_4.$$

This compound, which is likewise formed in other reactions, is derived from carbonic acid, $CO(OH)_2$, by substitution of 2 atoms of amidogen for 2 atoms of hydroxyl (see p. 264). It differs from carbamic acid in being a neutral substance, not containing any hydrogen easily replaceable by metals.

Other bibasic acids likewise yield an amic acid and a neutral amid by substitution of 1 or 2 atoms of amidogen for hydroxyl. Tribasic acids yield in like manner two amic acids and one neutral amide, and quadribasic acids may yield three amic acids and a neutral amide; thus, from pyrophosphoric acid, $P_2O_7H_4 = P_2O_3(OH)_4$, are obtained the three amic acids $P_2O_3(NH_2)(OH)_3$, $P_2O_3(NH_2)_2(OH)_2$, and $P_2O_3(NH_2)_3OH$.

Monobasic acids, which contain but one atom of hydroxyl, yield by this mode of substitution only neutral amides, no amic acids: thus from acetic acid, $C_2H_4O_2 = C_2H_3O(OH)$, is obtained acetamid, $C_2H_3O(NH_2)$.

By similar substitution of metals, or of basylous compound radicles, for the hydrogen of ammonia, basic compounds, called amines, are formed. Thus, when potassium is gently heated in ammonia gas, *monopotassamine*, NH_2K, is formed. It is an olive-green substance, which is decomposed by water into ammonia and potassium hydroxide:—

$$NH_2K + H_2O = NH_3 + KHO.$$

It melts at a little below 100°, and when heated in a close vessel, is as resolved into ammonia and *tripotassamine*:—

$$3NH_2K = 2NH_3 + NK_3.$$

The latter effervesces violently with water, yielding ammonia and potassium hydroxide:—

$$NK_3 + 3H_2O = NH_3 + 3KHO.$$

Metallammoniums.—These are hypothetical radicles derived from ammoniums $(NH_4)_n$, by substitution of metals for hydrogen. Salts of such radicles are formed in several ways. Ammonia gas is absorbed by various metallic salts in different proportions, forming compounds, some of which may be formulated as salts of metallammoniums. Thus, platinous chloride, $PtCl_2$, absorbs two molecules of ammonia, forming *platosammonium chloride*, $N_2H_6Pt''Cl_2$, and platinum tetrachloride, $PtCl_4$, absorbs four molecules of ammonia, forming *platinammonium chloride*, $N_4H_{12}Pt^{iv}Cl_4$. In like manner, cupric chloride and sulphate form the *chloride* and *sulphate of cuprammonium*, $N_2H_6Cu''Cl_2$, and $N_2H_6Cu''SO_4$.

Similar compounds are formed in many cases by precipitating metallic salts with ammonia or ammoniacal salts; thus, ammonia added to a solution of mercuric chloride, $HgCl_2$, forms a white precipitate, which may be represented as *mercurammonium chloride*, $NH_2Hg''Cl$; and by dropping solution of mercuric chloride into a boiling solution of sal-ammoniac mixed with free ammonia, crystals are obtained, consisting of *mercuriediammonium chloride*, $N_2H_6Hg''Cl_2$. Some of these compounds will be further considered in connection with the several metals.

METALS OF THE ALKALINE EARTHS.

The three metals, calcium, strontium, and barium, constituting this group, form oxides less soluble in water than the alkalis, but exhibiting similar taste, causticity, and action on vegetable colours. These metals form but one chloride, *e.g.*, $CaCl_2$; their carbonates are insoluble in water; and barium sulphate is also insoluble, the sulphates of calcium and strontium slightly soluble.

CALCIUM.

Symbol, Ca. Atomic weight, 40.

Calcium is one of the most abundant and widely diffused of the metals, though it is, of course, never found in the free state. As carbonate, it occurs in a great variety of forms, constituting, as limestone, entire mountain ranges.

Calcium was obtained in an impure state by Davy, by means similar to those adopted for the preparation of barium (*q.v.*). Matthiessen prepared the pure metal by fusing a mixture of two molecules of calcium chloride and one of strontium chloride with some chloride of ammonium in a small porcelain crucible, in which an iron cylinder is placed as positive pole, and a pointed iron wire or a little rod of carbon connected with the zinc of the battery is made to touch the surface of the liquid. The reduced metal fuses and drops off from the point of the iron wire, and the bead is removed from the liquid by a small iron spatula. Liès-Bodart and Gobin prepare calcium by igniting the iodide with an equivalent quantity of sodium in an iron crucible having its lid screwed down.

Calcium is a light yellow metal of sp. gr. 1·5778. It is about as hard as gold, very ductile, and may be cut, filed, or hammered out into plates as thin as the finest paper. It tarnishes slowly in dry, more quickly in damp air, decomposes water quickly, and is still more rapidly acted upon by dilute acids. Heated on platinum foil over a spirit-lamp, it burns with a bright flash; with a brilliant light also when heated in oxygen or chlorine gas, or in vapour of bromine, iodine, or sulphur.

Calcium Chloride, $CaCl_2$, is usually prepared by dissolving marble in hydrochloric acid; it is also a bye-product in several chemical manufactures. It separates from a strong solution in colourless, prismatic, and exceedingly deliquescent crystals, which contain six molecules of water. By heat this water is expelled, and by a temperature of strong ignition the salt is fused. The crystals

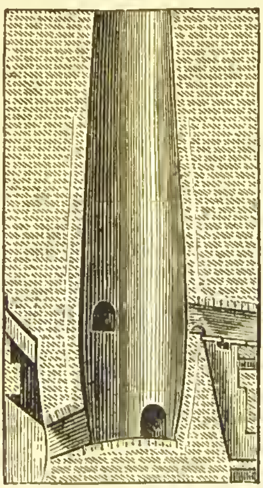
reduced to powder are employed in the production of artificial cold by being mixed with snow or powdered ice; and the chloride, strongly dried, or in the fused state, is of great use in desiccating gases, for which purpose the latter are slowly transmitted through tubes filled with fragments of the salt. Calcium chloride is also freely soluble in alcohol, which, when anhydrous, forms with it a definite crystallisable compound.

The *bromide*, $CaBr_2$, and *iodide*, CaI_2, closely resemble the chloride.

Calcium Fluoride, Fluor-Spar, CaF_2, is important as the most abundant natural source of hydrofluoric acid and the other fluorides. It occurs beautifully crystallised, of various colours, in lead-veins, the crystals having commonly the cubic, but sometimes the octahedral form, parallel to the faces of which latter figure they always cleave. Some varieties, when heated, emit a greenish, and some a purple phosphorescent light. The fluoride is quite insoluble in water, and is decomposed by oil of vitriol in the manner already mentioned (p. 108). $CaF_2 + H_2SO_4 = 2HF + CaSO_4$.

Calcium Oxides.—The *Monoxide* or *Lime*, CaO, may be obtained in a state of considerable purity by heating to full redness for some time fragments of white or black marble, or, better, of Iceland spar. If required absolutely pure, it must be made by igniting to whiteness, in a platinum crucible, an artificial calcium carbonate, prepared by precipitating the nitrate with ammonia carbonate. Lime in an impure state is prepared for building and agricultural purposes by calcining, in a kiln (fig. 131), the ordinary limestones which abound in many districts; a red heat, continued for some hours, is sufficient to disengage the whole of the carbon dioxide. In the best contrived lime-kilns the process is carried on continuously, broken limestone and fuel being constantly thrown in at the top, and the burned lime raked out at intervals from beneath. Sometimes, when the limestone contains silica, and the temperature has been very high, the lime refuses to slake, and is said to be *overburned*; in this case a portion of silicate has been formed.

Fig. 131.



Pure lime is white, and often very hard: it is quite infusible except in the electric furnace. At a high temperature it emits a dazzling white light. When moistened with water, it slakes with great violence, evolving heat, and crumbling to a soft, white, bulky powder, which is a hydrate containing a single molecule of water, which can be again expelled by a red heat. This

hydrate or hydroxide, CaH_2O_2 or CaO,H_2O, is soluble in water, but far less so than either the hydroxide of barium or of strontium, and, what is very remarkable, the *colder* the water, the larger is the quantity of the compound that is taken up. A pint of water at 15·5° dissolves about 11 grains, while at 100° only 7 grains are retained in solution. The hydroxide has been obtained in thin delicate crystals by slow evaporation under the air-pump. Lime-water is always prepared for chemical and pharmaceutical purposes by agitating cold water with excess of calcium hydroxide in a closely-stopped vessel, and then, after subsidence, pouring off the clear liquid, and adding a fresh quantity of water, for another operation. Lime-water has a strong alkaline reaction, a nauseous taste, and when exposed to the air becomes almost instantly covered with a pellicle of carbonate, by absorption of carbonic acid. It is used, like baryta-water, as a test for carbonic acid, and in medicine. Lime-water prepared from some varieties of limestone may contain traces of alkalis and silica.

The hardening of mortars and cements is in a great measure due to the gradual absorption of carbonic acid; but even after a very great length of time, this conversion into carbonate is not complete. Mortar is known, under favourable circumstances, to acquire extreme hardness with age. Lime cements which resist the action of water contain iron oxides, silica, and alumina; they require to be carefully prepared, the stone not being over-heated. When they are ground to powder and mixed with water, solidification speedily ensues, from causes not yet thoroughly understood, and the cement, once in this condition, is unaffected by wet. Roman cement is made in this manner from the nodular masses of calcareo-argillaceous ironstone found in the London clay.

Lime is of great importance in agriculture; it is found more or less in every fertile soil, and is often very advantageously added by the cultivator. The decay of vegetable fibre in the soil is thereby promoted, and other important objects, as the destruction of certain hurtful compounds in marsh and peat land, are often attained. The addition of lime probably serves likewise to liberate potassium from the insoluble silicate of that base contained in the soil.

Experiment.—1. Place a mass of good lime (2 or 3 ounces) on a plate, and pour on a small quantity of hot water. After a few minutes the mass gives off steam and breaks up. Add small quantities of hot water as long as it is absorbed. Lime requires, theoretically, about one-third of its weight of water ($CaO:H_2O=56:18$) for the production of the hydrate.

Stir up the slaked lime in half a gallon of water contained in a Winchester quart, let the mixture stand till clear, and preserve the lime-water for use.

2. Place small quantities of solutions of silver nitrate, ferric chloride, mercuric chloride, in separate beakers, and add to each an excess of lime-water, and note the colour of the precipitated oxides.

Calcium Dioxide, CaO_2, is obtained, in microscopic crystals, having the composition $CaO_2,8H_2O$, by precipitating lime-water with hydrogen dioxide.

Chloride of Lime, Bleaching Powder.—When calcium hydroxide, very slightly moist, is exposed to chlorine gas, the latter is absorbed, and a compound is produced—the bleaching powder of commerce—which is used on an immense scale for bleaching linen and cotton goods. At the commencement of the process, the chlorine must be supplied slowly, so as to avoid rise of temperature. The product, when fresh and well prepared, is a soft white powder which attracts moisture slowly from the air, and exhales an odour sensibly different from that of chlorine. It is soluble in about 10 parts of water, the unaltered hydroxide being left behind: the solution is highly alkaline, and bleaches feebly. When calcium hydroxide is suspended in cold water, and chlorine gas transmitted through the mixture, the lime is gradually dissolved, and the same peculiar bleaching compound produced; the alkalis also, either caustic or carbonated, may by similar means be made to absorb a large quantity of chlorine, and give rise to corresponding compounds: such are the "disinfecting solutions" of Labarraque.

The composition of bleaching powder is represented by the formula $CaOCl_2$, and it was formerly supposed to be a direct compound of lime with chlorine. This view, however, is not consistent with its reactions, for when distilled with dilute nitric acid, it readily yields a distillate of aqueous hypochlorous acid, and when treated with water it is resolved into chloride and hypochlorite of calcium, the latter of which may be separated in crystals by exposing the filtered solution to a freezing mixture, or by evaporating it in a vacuum over oil of vitriol, and leaving the dense frozen mass to thaw upon a filter. A solution of calcium chloride mixed with hypochlorite then passes through, and feathery crystals remain on the filter, very unstable, but consisting, when recently prepared, of hydrated calcium hypochlorite, $Ca(OCl)_2,4H_2O$ (Kingzett). These results seem at first sight to show that the bleaching powder is a mixture of chloride and hypochlorite of calcium, formed according to the equation,

$$2CaO + 2Cl_2 = CaCl_2 + CaCl_2O_2;$$

but if this were its true constitution, the powder, when digested with alcohol, ought to yield a solution of calcium chloride containing half the chlorine of the original compound, which is not the case. Its constitution is therefore better represented by the formula Cl.Ca.OCl, suggested by Odling, this molecule being decomposed by water into chloride and hypochlorite in the manner just explained, and yielding, with dilute nitric acid, a distillate containing hypochlorous acid:—

$$Ca(ClO)_2 + 2HNO_3 = Ca(NO_3)_2 + 2HClO.$$

When the temperature of the calcium hydroxide has risen during the absorption of the chlorine, or when the compound has been subsequently exposed to heat, its bleaching properties are impaired or altogether destroyed : it then contains chlorate and chloride of calcium :—

$$6CaCl.ClO = 5CaCl_2 + Ca(ClO_3)_2.$$

The same change seems to ensue by long keeping, even at the common temperature of the air. In an open vessel the compound is speedily decomposed by the carbonic acid of the air, hypochlorous acid being evolved. Commercial bleaching powder thus constantly varies in value with its age, and with the care originally bestowed upon its preparation : the best may contain about 30 per cent. of available chlorine, easily liberated by an acid, which is, however, far short of the theoretical quantity.

The general method in which this substance is employed for bleaching is the following :—The goods are first immersed in a dilute solution of chloride of lime, and then transferred to a vat containing dilute sulphuric acid. Decomposition ensues ; the calcium both of the hypochlorite and of the chloride is converted into sulphate, while the hypochlorous and hydrochloric acids yield water and free chlorine :—

$$CaOCl_2 + H_2SO_4 = CaSO_4 + HClO + HCl, \text{ and}$$
$$HClO + HCl = H_2O + Cl_2.$$

The chlorine thus disengaged in contact with the cloth causes destruction of the colouring matter. The process is repeated several times, since it is unsafe to use strong solutions.

On the same principle, white patterns are imprinted upon coloured cloth, the figures being stamped with tartaric acid thickened with gum-water, and then the stuff immersed in the chlorine bath, when the parts to which no acid has been applied remain unaltered, while the printed portions are bleached.

For purifying an offensive or infectious atmosphere, *as an aid to proper ventilation*, the bleaching powder is very convenient. The solution is exposed in shallow vessels, or cloths steeped in it are suspended in the apartment, when the carbonic acid of the air slowly decomposes it in the manner above described. Addition of a strong acid causes rapid disengagement of chlorine.

The value of any sample of bleaching powder may be estimated by its effect in oxidising a ferrous salt to ferric salt, 2 molecules of ferrous salt requiring for the purpose 2 atoms of chlorine, according to the equation : $2FeSO_4 + H_2SO_4 + Cl_2 = 2HCl + Fe_2(SO_4)_3$. To make the estimation, 0·784 gram of pure crystallised ferrous sulphate is dissolved in water, a little sulphuric acid is added, and the solution of bleaching powder is dropped in from a burette till the ferrous salt is converted into ferric salt. The completion of the reaction is ascertained by bringing a drop of the solution, together with a drop of potassium ferricyanide, on a white plate, until no

further coloration is observed. A simple calculation gives the result, the above quantity of ferrous sulphate, $FeSO_4,7H_2O$, being equivalent to 0·1 gram of chlorine.

Experiment.—1. Dissolve an ounce of bleaching powder in about a pint of water, and filter the liquid. Dip into it a piece of red calico print, notice that the colour slowly fades. Now take a piece of the same print, wet it first with dilute sulphuric acid, and then dip it into the bleaching liquid ; the colour will disappear immediately.

2. Add a little of the solution to solutions of lead nitrate and manganese chloride or sulphate. Dark-coloured precipitates are formed consisting of the peroxides of these metals, PbO_2 and MnO_2.

Calcium Sulphate, $CaSO_4$.—Crystalline native calcium sulphate, containing 2 molecules of water, is found in considerable abundance in some localities as *gypsum* : it is often associated with rock-salt. When regularly crystallised, it is termed *selenite.* Anhydrous calcium sulphate is also occasionally met with. The salt is formed by precipitation, when a moderately concentrated solution of calcium chloride is mixed with sulphuric acid. Calcium sulphate is soluble in about 500 parts of cold water, and its solubility is a little increased by heat. At 35° the solubility attains a maximum, and 1 part of the salt dissolves in 432 parts of water. The solubility is much increased when common salt or ammonium chloride is added to the solution, but it is much diminished by the addition of calcium chloride. But while the addition of common salt to the water increases the solubility of calcium sulphate till the proportion of salt to water is 20 or 25 to 100, a larger quantity diminishes the solubility of calcium sulphate. At 20° to 60°, 100 parts of water to which 20 parts of sodium chloride have been added dissolve 0·82 part of calcium sulphate, $CaSO_4$, which corresponds to rather more than 1 part of gypsum. At temperatures above 100° the solubility of calcium sulphate diminishes whether chlorides are present or not. Above 150° calcium sulphate is practically insoluble in pure water.

Gypsum, or native hydrated calcium sulphate, is largely employed for the purpose of making casts of statues and medals, also for moulds in the porcelain and earthenware manufactures, and for other applications. It is exposed to heat in an oven where the temperature does not exceed 127°, by which the greater part of the water of crystallisation is expelled, and it is afterwards reduced to a fine powder. When mixed with water, it solidifies after a short time, from the re-formation of the same hydrate ; but this effect does not happen if the gypsum has been over-heated. It is often called Plaster of Paris. Artificial coloured marbles, or *scagliola*, are frequently prepared by inserting pieces of natural stone in a soft stucco containing this substance, and polishing the surface when the cement has become hard. Calcium sulphate is one of the most common impurities of spring water.

The peculiar property water acquires by the presence of calcium salts is termed *hardness.* It manifests itself by the effect such waters

have upon the palate, and particularly by its peculiar behaviour with soap. Hard water yields a lather with soap only after the whole of the calcium salts have been thrown down from the water in the form of an insoluble lime-soap. The hardness produced by calcium sulphate is called *permanent hardness*, since it cannot be remedied by boiling the water. Calcium sulphate gives rise to a very hard crystalline scale upon the inner surface of steam boilers in which hard water is used. It also forms a crust upon the pans in which brine is boiled down for making common salt.

Calcium and Potassium Sulphate, $CaSO_4,K_2SO_4+H_2O$, is formed by the solutions of the two salts mixed together. An intimate mixture of equal weights of the anhydrous salts, stirred up with less than their weight of water, coagulates suddenly to a solid mass. With 4 to 5 parts of water, solidification takes place more slowly, and the mixture may be used for taking casts.—*Calcium and Sodium Sulphate*, $CaSO_4,Na_2SO_4$, occurs native as *glauberite*. Needle-shaped crystals, having the composition $CaSO_4,Na_2SO_4,2H_2O$, are obtained on mixing 1 part precipitated calcium sulphate and 50 parts Glauber's salt, and heating the mixture at 80° with 25 parts water. When further heated, they are transformed into small crystals of glauberite.

Calcium Nitrate, $Ca(NO_3)_2$.—This salt, prepared by dissolving chalk in nitric acid, forms in the anhydrous state a white porous deliquescent mass, very soluble in water and in alcohol. When heated and then exposed to sunshine, it appears luminous in the dark, and is hence called "Baldwin's Phosphorus," from the name of the alchemist Baldewein or Balduinus, who first prepared it. It is often found as an efflorescence on the walls of stables and other places through which urine or other organic liquids percolate: hence it has been called *lime-saltpetre* or *wall-saltpetre*.

Calcium Phosphates. — The *Tricalcic Salt*, $Ca_3(PO_4)_2$, occurs, combined with chloride and fluoride of calcium, in a p a t i t e, which crystallises in the rhombohedral system; and its massive varieties, *phosphorite* and *extremadurite*, which occur in Estremadura in Spain, have the composition $3Ca_3(PO_4)_2+CaF_2$, the fluorine being sometimes partly replaced by chlorine. Apatite is now also obtained in considerable quantities from Canada. Tricalcic phosphate occurs pure in o s t e o l i t e, a mineral found near Hanau and at Amberg in the Erzgebirge; also pure in o r n i t h i t e, a crystallised mineral found in the guano of Sombrero, a small island of the Antilles group; and mixed with an aluminium phosphate in s o m b r e r i t e, occurring also in the same islands. Tricalcic phosphate is also the chief mineral constituent of bones, in the ash of which it occurs to the amount of about 80 per cent., together with magnesium phosphate, calcium carbonate, and calcium fluoride.

Tricalcic phosphate is obtained as a white precipitate by adding disodic orthophosphate (ordinary phosphate of soda) to an ammo-

niacal solution of calcium chloride. It is nearly insoluble in water, but is decomposed by prolonged boiling with water into an insoluble basic salt, $Ca_3(PO_4)_2+Ca_2(PO_4)OH$, and a soluble acid salt. It dissolves also in water containing ammoniacal salts, chloride and nitrate of sodium, and other salts; easily also in all acids, even in aqueous carbonic acid.

Monocalcic Orthophosphate, $CaHPO_4$, separates with 2 molecules of water as a white crystalline precipitate, on treating a solution of calcium chloride with ordinary sodium phosphate. It occurs in urinary concretions, and is sometimes deposited from urine in rosettes or stellate groups of microscopic crystals.

Tetrahydro-calcic Phosphate, $H_4Ca(PO_4)_2$, separates in rhombic tablets, when a solution of either of the preceding salts in the requisite quantity of phosphoric acid is left to evaporate. By treatment with boiling water, it is converted into the anhydrous monocalcic salt, and with cold water into the same with $2H_2O$.

Superphosphate of Lime.—This name is applied to a mixture of monocalcic orthophosphate and calcium sulphate prepared on the large scale by treating bone-ash, coprolites, phosphorites, etc., with two-thirds of their weight of sulphuric acid. It is used for the preparation of phosphorus, and very largely as a manure, especially for root-crops.

Calcium Hypophosphite, $Ca(PO_2H_2)_2$, a salt used in medicine, is prepared by boiling phosphorus with milk of lime, and separates from the clear solution on evaporation in bright flexible four-sided prisms, insoluble in alcohol.

Calcium Carbonate, *Chalk; Limestone; Marble;* $CaCO_3$.—Calcium carbonate, often more or less contaminated with iron oxide clay, and organic matter, forms rocky beds, of immense extent and thickness, in almost every part of the world. These present the greatest diversities of texture and appearance, arising, partly from changes to which they have been subjected since their deposition. The most ancient and highly crystalline limestones are destitute of visible organic remains, while those of more recent origin are often entirely made up of the shelly exuviæ of once-living beings. Sometimes these latter are of such a nature as to show that the animals inhabited fresh water; marine species and corals are, however, most abundant. Cavities in limestone and other rocks are very often lined with magnificent crystals of calcium carbonate or calcareous spar, which have evidently been slowly deposited from a watery solution. Calcium carbonate is always precipitated when an alkaline carbonate is mixed with a solution of a calcium salt.

Although this substance is not sensibly soluble in pure water, it is freely taken up when carbonic acid happens at the same time to be present. If a little lime-water be poured into a vessel of carbon dioxide gas, the turbidity first produced disappears on agitation, and a transparent solution of calcium carbonate in excess of carbonic acid

is obtained. This solution is decomposed completely by boiling, the carbonic acid being expelled, and the carbonate precipitated. Since all natural waters contain dissolved carbonic acid, it is to be expected that calcium in this state should be of very common occurrence ; and such is really found to be the fact, river, and more especially spring water, almost invariably containing calcium carbonate thus dissolved. In limestone districts this is often the case to a great extent. The *hardness* of water due to the presence of calcium carbonate, is called *temporary*, since it is diminished to a very considerable extent by boiling, and may be nearly removed by mixing the hard water with lime-water, when both the dissolved carbonate and the dissolved lime, which thus becomes carbonated, are precipitated. Upon this principle Clark's process of softening water is based. This process is of considerable importance, since a supply of hard water to towns is in many respects a source of great inconvenience. As already mentioned, the use of such water, for the purposes of washing, is attended with a great loss of soap. Boilers, in which such water is heated, speedily become lined with a thick stony incrustation, The beautiful stalactitic incrustations of limestone caverns, and the deposit of calc-sinter or travertin upon various objects, and upon the ground, in many places, are explained by the solubility of calcium carbonate in water containing carbonic acid.

Experiment. — 1. Pass CO_2 from the usual apparatus through clear lime-water, noting the formation of the precipitate of calcium carbonate. Continue passing in the gas till the precipitate has redissolved. The resulting solution may be taken to represent a water having considerable temporary hardness.

2. To a portion of this solution add an equal bulk of clear lime-water. A white precipitate is formed containing the whole of the lime, leaving the water soft.

3. Boil a portion of the same solution for five minutes. A gritty precipitate of $CaCO_3$ is deposited, and the water is rendered soft.

4. Place in a clear stoppered bottle 50 cubic centimetres of distilled water and add to it a small measured quantity, say 5 c.c., of soap-test.* Shake the bottle, and observe that the liquid forms a permanent froth or lather.

5. Make the same experiment, using water from the tap. Nearly all common waters will require a larger quantity of soap before a permanent lather is produced on shaking. A comparison may thus be made between different waters, and a rough estimate formed of the quantity of calcium and magnesium salts they contain.

Crystallised calcium carbonate is dimorphous ; calc-spar and arragonite, although possessing exactly the same chemical composition, have different crystalline forms, different densities, and different optical properties. Calcium carbonate appears in the form of calc-

* This is a solution of a neutral soap in weak spirit of wine. It may be purchased of the right strength, or may be made according to instructions given in most works on quantitative analysis.

spar when deposited from its solution in water containing carbonic acid at the ordinary temperature. At 90°, however, and at the boiling temperature, it is chiefly deposited in the form of arragonite; at lower temperatures the formation of arragonite decreases, whilst that of calc-spar increases, the limit for the formation of the former variety being between 30° and 50°.

Calc-spar occurs very abundantly in crystals derived from an obtuse rhombohedron, whose angles measure 105° 5′ and 74° 55′: its density varies from 2·5 to 2·8. The rarer variety, or arragonite, is found in crystals whose primary form is a right rhombic prism, a figure having no geometrical relation to the preceding: it is, besides, heavier and harder. Density = 2·92 to 3·28.

Calcium Sulphides.—The monosulphide, CaS, is obtained by reducing the sulphate at a high temperature with charcoal or hydrogen: it is nearly colourless, and but little soluble in water. By boiling together calcium hydrate, water, and flowers of sulphur, a red solution is obtained, which, on cooling, deposits crystals of the bisulphide, CaS_2, containing water. When the sulphur is in excess, and the boiling long continued, a pentasulphide is generated: a thiosulphate is also formed during these reactions:—

$$3CaO + S_6 = 2CaS_2 + CaS_2O_3.$$

When the yellow solution obtained by boiling lime with excess of sulphur is poured out into an excess of hydrochloric acid, sulphur is precipitated together with hydrogen persulphide (p. 125); but if the acid be poured into the solution of calcium sulphide, gaseous hydrogen sulphide is given off, and the precipitate formed consists wholly of finely-divided sulphur, the *sulphur precipitatum* of the Pharmacopœia. If dilute sulphuric acid is used, the precipitate also contains gypsum.

The "waste" left after the "black ash" of the alkali-maker has been exhausted with water consists partly of limestone and coke and partly of calcium monosulphide, which usually constitutes about 40 per cent. of the whole. The accumulation of heaps of this material at the alkali works represents a serious loss to the manufacturer, besides annoyance to the neighbourhood. Rain falling upon the heaps brings down oxygen and carbonic acid, and the water which runs off into the streams or drains contains a quantity of the more soluble polysulphides of calcium. These compounds, meeting acid waste liquors from other processes, or even under the action of the carbonic acid of the air, give off hydrogen sulphide gas.

One of the most successful modes of dealing with the drainage water consists in oxidising the yellow liquid by air, assisted by steam, until, on testing a portion of the liquid with hydrochloric, no sulphuretted hydrogen is evolved, and the whole of the sulphur is precipitated. The liquid in this state contains calcium polysulphides, together with thiosulphate, and the action of the acid is represented as follows:—

$$2CaS_{1+x} + CaS_2O_3 + 6HCl = 3CaCl_2 + 3H_2O + (4+x)S.$$

The sulphur is allowed to settle, and the clear solution of calcium chloride drained off.

But the cost of hydrochloric acid is too great to permit of the application of this method to the whole of the waste as it is taken from the tanks, and various attempts have been made to deal with it profitably. Of these, two processes may be mentioned in outline.

1. The process of Schaffner and Helbig. In this the fresh waste is treated with strong solution of magnesium chloride, whereby pure H_2S is evolved :—

$$CaS + MgCl_2 + H_2O = CaCl_2 + MgO + H_2S.$$

The gas is conveyed away, and either treated separately for the recovery of the sulphur or it is burnt, and the products conveyed into an ordinary lead chamber for making vitriol. The next step is to expose the residual mixture of calcium chloride and magnesia to the action of carbonic acid gas under slight pressure :—

$$MgO + CaCl_2 + CO_2 = MgCl_2 + CaCO_3.$$

The magnesium chloride is thus regenerated for use in a subsequent operation, and the calcium carbonate which is precipitated is strained off, and used in making black ash.

This process, in the hands of Messrs Chance Brothers, was a complete success as a manufacturing operation, but commercial considerations, chiefly connected with the fall in price of pyrites, led to its abandonment.

2. *Chance's Process.*—This has been made the subject of a patent, and is now in successful operation. It has been described on pp. 118, 119.

Calcium Phosphide.—When vapour of phosphorus is passed over fragments of lime heated to redness in a porcelain crucible, a chocolate-brown compound, the so-called *phosphuret of lime*, is produced. This substance is probably a mixture of calcium phosphide and phosphate. When thrown into water, it yields spontaneously inflammable hydrogen phosphide. According to Paul Thenard, the calcium phosphide in this compound has the composition P_2Ca_2. In contact with water it yields liquid hydrogen phosphide, P_2H_4 (p. 173)

$$P_2Ca_2 + 2H_2O = 2CaO + P_2H_4 :$$

and the greater portion of this liquid phosphide is immediately decomposed into solid and gaseous hydrogen phosphide : $5P_2H_4 = P_4H_2 + 6PH_3$.

Calcium Carbide, CaC_2.—This compound is obtained by heating a mixture of lime and charcoal in an electric furnace, an arrangement by which a substance may be exposed in a carbon crucible to the temperature of the electric arc, produced by bringing together two carbon electrodes of which one may be the bottom of the crucible itself.

Calcium carbide is a dark coloured substance which in contact with water is decomposed, yielding acetylene (p. 194) and is now manufactured on a considerable scale for the production of this gas as an illuminant.

For the tests used in the detection and recognition of calcium salts, see p. 394.

For the spectroscopic behaviour of calcium salts, see the coloured plate.

STRONTIUM.

Symbol, Sr. Atomic weight, 87·3.

This element occurs as carbonate in the mineral called *Strontianite*, found at Strontian, in Argyleshire, also as sulphate or *Cœlestin*; in small quantity, as chloride or sulphate in many brine-springs and mineral waters, in sea-water, and in the ash of *Fucus vesiculosus*.

Metallic strontium was discovered by Davy, who obtained it by electrolysis of the moistened oxide or of the aqueous chloride, but it is more readily prepared by electrolysis of the fused anhydrous chloride. A small porcelain crucible having a porous cell is filled with strontium chloride mixed with a little sal-ammoniac; a fine iron wire placed within the cell constitutes the negative pole, and the postive pole is an iron cylinder placed in the crucible round the cell. The heat is regulated so that a crust forms in the cell, and the metal collects under this crust (Matthiessen).

Strontium is a yellow metal, somewhat harder than calcium, malleable, and having a density 2·5. It melts at a red heat, oxidises quickly in the air, burns brilliantly when heated, and decomposes water at common temperatures.

Strontium Chloride, $SrCl_2$, prepared by dissolving the carbonate in hydrochloric acid, crystallises in colourless needles or prisms, $SrCl_2,6H_2O$, which are slightly deliquescent, dissolved in 2 parts of cold, and in a smaller quantity of boiling water; also in alcohol, forming a solution which burns with a crimson flame.

Oxides.—The *Monoxide* or *Strontia*, prepared by ignition of the nitrate, is a greyish-white porous infusible mass. It unites readily with a small quantity of water, forming a white powder of strontium hydroxide, $Sr(OH)_2$, which dissolves readily in hot water, and separates on cooling as a hydrate, $Sr(OH)_2,8H_2O$, soluble in 50 parts cold, and 2·4 of boiling water. The solution is alkaline and caustic, but less so than those of the alkalis or of baryta. Strontia acquired a few years ago some importance from its employment in connection with the refining of sugar.

The *Dioxide*, SrO_2, is prepared by the action of hydrogen dioxide

on strontia-water, and separates in pearly scales containing 2 molecules of water, which they give off when heated.

Strontium Sulphate, $SrSO_4$, occures native in rhombic crystals and fibrous masses sometimes having a light blue colour: hence called *cœlestin.* The same compound is thrown down as a white precipitate, sp. gr. 3·707, when sulphuric acid or a soluble sulphate is added to a solution of a strontium salt. It is intermediate in solubility between the sulphates of calcium and barium, and less soluble in boiling than in cold water.

Strontium Nitrate, $Sr(NO_3)_2$, crystallises in anhydrous octahedrons, soluble in 5 parts of cold, and about half their weight of boiling water. It is chiefly of value to the pyrotechnist, who employs it in the composition of the well known "red fire."*

Strontium Carbonate, $SrCO_3$, occurs as strontianite in crystals isomorphous with those of arragonite, and is obtained by precipitation as a white impalpable powder, having a density of 3·62. When boiled with sal-ammoniac, it is converted into the chloride.

All strontium compounds impart a deep crimson colour to the flame of alcohol. Their spectral reactions have been already noticed (p. 333), see also the coloured plate. For their reactions with liquid reagents, see page 394.

BARIUM.

Symbol, Ba. Atomic weight, 137.

The name Barium is derived from βαρύς, heavy, in allusion to the great density of the native carbonate and sulphate.

This metal occurs abundantly as sulphate and carbonate, forming the *veinstone* in many lead mines. Davy obtained it in the metallic state by electrolysis of a salt of barium using mercury as the negative electrode, or by electrolysing hydrate of barium mixed with oxide of mercury. In either case an amalgam is obtained from which the mercury can afterwards be expelled by heat. Bunsen subjected barium chloride mixed to a paste with water and a

* RED FIRE:	Grains.	GREEN FIRE:	Grains.
Dry strontium nitrate,	800	Dry barium nitrate,	450
Sulphur,	225	Sulphur,	150
Potassium chlorate,	200	Potassium chlorate,	100
Lampblack,	50	Lampblack,	25

The strontium or barium-salt, the sulphur, and the lampblack must be finely powdered and intimately mixed, after which the potassium chlorate should be added in rather coarse powder, without rubbing, with the other ingredients. The red fire composition has been known to ignite spontaneously.

little hydrochloric acid, at a temperature of 100°, to the action of the electric current, using an amalgamated platinum wire as the negative pole. In this manner the metal was obtained as a solid, highly crystalline amalgam, which, when heated in a stream of hydrogen, yielded barium in the form of a tumefied mass, tarnished on the surface, but often exhibiting a silver-white lustre in the cavities. Barium may also be obtained, though impure, by passing vapour of potassium over the red-hot chloride or oxide of barium. It is malleable, melts below a red heat, decomposes water, and gradually oxidises in the air.

Barium Chloride, $BaCl_2,2H_2O$, is prepared by dissolving the native carbonate in hydrochloric acid, filtering the solution, and evaporating until a pellicle begins to form at the surface: the solution on cooling deposits crystals. When native carbonate cannot be procured, the native sulphate may be employed in the following manner:—It is reduced to fine powder, and intimately mixed with one-third of its weight of powdered coal: the mixture is pressed into an earthen crucible to which a cover is fitted, and exposed for an hour or more to a red heat, by which the sulphate is converted into sulphide at the expense of the combustible matter of the coal; the black mass thus obtained is powdered and boiled in water, by which the sulphide is dissolved; and the solution, filtered hot, is mixed with a slight excess of hydrochloric acid. Barium chloride and hydrogen sulphide are then produced, the latter escaping with effervescence. Lastly, the solution is filtered to separate any little insoluble matter, and evaporated to the crystallising point.

The crystals of barium chloride are flat four-sided tables, colourless and transparent. They contain two molecules of water, easily driven off by heat. 100 parts of water dissolve 43·5 parts at 15·5°, and 78 parts at 104·5°, which is the boiling point of the saturated solution.

Barium Oxides.—The *Monoxide* or *Baryta*, BaO, is best prepared by decomposing the crystallised nitrate by heat in a capacious porcelain crucible until red vapours are no longer disengaged: the nitrate is then resolved into nitric peroxide, oxygen and baryta, which remains behind in the form of a greyish spongy mass, fusible at a high temperature. When moistened with water it combines into a hydrate, with great elevation of temperature. The *Hydroxide* or *Hydrate*, $BaH_2O_2 = BaO,H_2O$, is prepared on the large scale by decomposing a hot concentrated solution of barium chloride with a solution of caustic soda; on cooling, crystals of barium hydrate are deposited, which may be purified by recrystallisation. In the laboratory barium hydrate may be prepared by boiling a strong solution of the sulphide with small successive portions of black oxide of copper until a drop of the liquid ceases to form a black precipitate with lead salts: the filtered liquid on cooling yields crystals of the hydrate. The crystals of barium hydrate contain $BaH_2O_2,8H_2O$; they fuse

easily, and lose their water of crystallisation when strongly heated, leaving the hydroxide, BaH_2O_2, in the form of a white, soft powder, which readily absorbs carbon dioxide when exposed to the air, and is soluble in 20 parts of cold and 2 parts of boiling water. The solution is a valuable reagent: it is highly alkaline to test-paper, and instantly rendered turbid by the smallest trace of carbonic acid.

The *Dioxide*, BaO_2, may be formed as already mentioned, by exposing baryta, heated to full redness in a porcelain tube, to a current of pure oxygen gas. It is grey, and forms with water a white hydrate, which is not decomposed by that liquid in the cold, but dissolves in small quantity. Barium hydroxide, when heated to redness in a current of dry atmospheric air, gives off water, and is converted, by absorption of oxygen, into barium dioxide, from which the second atom of oxygen may be expelled at a higher temperature. These reactions are utilised for the preparation of oxygen upon a large scale (p. 35). The dioxide may also be made by heating pure baryta to redness in a platinum crucible, and then gradually adding an equal weight of potassium chlorate, whereby barium dioxide and potassium chloride are produced. The latter may be extracted by cold water, and the dioxide left in the state of hydrate. It is used for the preparation of hydrogen dioxide (p. 226). When dissolved in dilute acid, it is decomposed by potassium dichromate, and by the oxide, chloride, sulphate, and carbonate of silver.

Oxysalts of Barium.—The *Nitrate*, $Ba(NO_3)_2$, is prepared by methods exactly similar to those adopted for preparing the chloride, nitric acid being substituted for hydrochloric. It crystallises in transparent colourless anhydrous octahedrons, requiring for solution 8 parts of cold and 3 parts of boiling water. This salt is much less soluble in dilute nitric acid than in pure water. Errors sometimes arise from such a precipitate of crystalline barium nitrate being mistaken for sulphate. It disappears on heating, or by addition of water.

The *Sulphate*, $BaSO_4$, is found native as *heavy spar* or *barytes*, often beautifully crystallised: its density is as high as 4·4 to 4·8. This compound is always produced when sulphuric acid or a soluble sulphate is mixed with a solution of a barium salt. It is not sensibly soluble in water or in dilute acids: even in nitric acid it is almost insoluble; hot oil of vitriol dissolves a little, but the greater part separates again on cooling. Barium sulphate is produced artificially on a large scale, and is used as a substitute for white lead in the manufacture of oil-paints. The sulphate to be used for this purpose is precipitated from very dilute solutions: it is known in commerce as *blanc fixe*. Powdered native barium sulphate, being rather crystalline, has not sufficient body. For the production of sulphate, the chloride of barium is first prepared, which is dissolved in a large quantity of water, and then precipitated by dilute sulphuric acid.

The *Carbonate*, $BaCO_3$, is found native as *witherite*, and may be

formed artificially by precipitating the chloride or nitrate with an alkaline carbonate, or carbonate of ammonia. It is a heavy, white powder, very sparingly soluble in water, and chiefly useful in the preparation of other barium salts.

Barium Sulphides.—The *Monosulphide*, BaS, is obtained in the manner already described (p. 392); the higher sulphides may be formed by boiling it with sulphur. Barium monosulphide crystallises from a hot solution in thin, nearly colourless plates, which contain water, and are not very soluble: they are rapidly altered by the air. A strong solution of this sulphide may be employed, as already described, in the preparation of barium hydroxide.

Reactions of the Alkaline Earth-Metals in Solution.—Barium, strontium, and calcium are distinguished from all other substances, and from each other, by the following characters:—

Caustic potash, when free from carbonate, and caustic *ammonia*, occasion no precipitates in *dilute* solutions of the alkaline earths, especially of the last two, the hydrates being soluble in water.

Alkaline carbonates, and *carbonate of ammonia*, give white precipitates, insoluble in excess of the precipitant, with all three.

Sulphuric acid, or a *sulphate*, added to very dilute solutions of the salts of these metals, gives an immediate white precipitate with barium salts; and a similar precipitate after a short interval with strontium salts; no change with calcium salts. The precipitates with barium and strontium salts are insoluble in nitric acid.

Solution of *calcium sulphate* gives an instantaneous cloud with barium salts; also with strontium salts after a little time.

Strontium sulphate is itself sufficiently soluble to occasion turbidity when mixed with barium chloride.

Lastly, the soluble *oxalates* give, in the most dilute solutions of calcium salts, a white precipitate, which is not dissolved by a drop or two of hydrochloric, or by an excess of acetic acid. This is an exceedingly characteristic test.

The *chlorides of strontium* and *calcium* dissolved in alcohol, colour the flame of the latter red or purple: *barium salts* communicate to the flame a pale green tint.

Silicofluoric acid gives a white precipitate with barium salts, none with salts of strontium or calcium.

METALS OF THE MAGNESIUM GROUP.

Beryllium.	Zinc.
Magnesium.	Cadmium.

THESE metals are all diads. They are volatile, and burn brightly when heated in the air. They decompose water at high temperatures only, but dissolve readily at ordinary temperatures in hydrochloric and dilute sulphuric acid, with evolution of hydrogen. Each forms only one oxide and one sulphide. The sulphates are soluble in water; the oxides, the normal carbonates, and the phosphates are insoluble.

BERYLLIUM, or GLUCINUM.

Symbol, Be. Atomic weight, 9·1.

This somewhat rare metal occurs as a silicate, either alone as in phenacite, or associated with other silicates, in beryl, emerald, euclase, leucophane, helvite, and several varieties of gadolinite; also as an aluminate in chrysoberyl or cymophane.

Metallic beryllium is obtained by passing the vapour of the chloride over melted sodium. It is a white, hard crystalline metal of density 1·85; its melting point is below that of silver. It does not decompose boiling water. Sulphuric and hydrochloric acids dissolve it, with evolution of hydrogen.

Beryllium forms but one class of compounds, its chloride being $BeCl_2$, its oxide BeO.

There has been much discussion as to the atomic weight of this element, but the specific heat of the nearly pure metal has been found to be approximately ·62, which, multiplied by the atomic weight, 9·1, gives a product, 5·64, as the atomic heat (see p. 248).

Beryllium Chloride, $BeCl_2$, is formed by heating the metal in chlorine or hydrochloric acid gas, or by the action of aqueous hydrochloric acid on the metal or its oxide.

The anhydrous chloride is prepared by passing chlorine over an ignited mixture of berylla and charcoal. It is less volatile than aluminium chloride, very deliquescent, and easily soluble in water.

The vapour-density at temperatures from 685° to 1500° has been found to be 40·9, which agrees with the formula $BeCl_2$.

Beryllium Oxide.—Berylla, BeO.—This earth may be prepared from beryl, or either of the other beryllium silicates, by fusing the finely pounded mineral with potassium carbonate or quicklime;

treating the fused mass with hydrochloric acid; evaporating to dryness; then moistening the residue with hydrochloric acid, and treating it with water, whereby everything is dissolved except the silica. The filtered liquid is then mixed with excess of ammonia solution, which throws down a bulky precipitate containing both alumina and berylla; this precipitate is well washed, and the berylla is dissolved out from the alumina by digestion in a cold strong solution of ammonium carbonate. The liquid is again filtered, and on boiling it, beryllium carbonate is deposited as a white powder, which, when ignited, leaves pure berylla.

Berylla is very much like alumina in physical characters, and further resembles that substance in being readily dissolved by caustic potash or soda; but it is distinguished from alumina by its solubility, when recently precipitated, in a cold solution of ammonium carbonate. Beryllium salts have a sweet taste, whence the former name of the metal, *glucinum* (from γλυκὺς). They are colourless, and are distinguished from those of aluminium by not yielding an alum with potassium sulphate, or a blue colour when heated before the blowpipe with cobalt nitrate; also by their reaction with ammonium carbonate.

MAGNESIUM.

Symbol, Mg. Atomic weight, 24.

This metal was formerly classed with the metals of the alkaline earths, but it is much more nearly related to zinc by its properties in the free state, as well as by the volatility of its chloride, the solubility of its sulphate, and the isomorphism of several of its compounds with the similarly constituted compounds of zinc.

Magnesium occurs in the mineral kingdom as hydroxide, carbonate, borate, phosphate, sulphate, and nitrate, sometimes in the solid state, sometimes dissolved in mineral waters: magnesian limestone, or dolomite, which forms entire mountain masses, is a carbonate of magnesium and calcium. Magnesium also occurs as silicate, combined with other silicates, in a variety of minerals, as steatite, hornblende, augite, talc, etc.; also as aluminate in spinelle and zeilanite. It likewise occurs in the bodies of plants and animals, chiefly as carbonate and phosphate, and in combination with organic acids.

Metallic magnesium is prepared:

1. By the electrolysis of fused magnesium chloride, or, better, of a mixture of 4 molecules of magnesium chloride and 3 molecules of potassium chloride with a small quantity of sal-ammoniac. A convenient way of effecting the reduction is to fuse the mixture in a common clay tobacco-pipe over an Argand spirit-lamp or gas-burner,

the negative pole being an iron wire passed up the pipe-stem, and the positive pole a piece of gas-coke, just touching the surface of the fused chlorides. On passing the current of a battery of ten Bunsen's cells through the arrangement, the magnesium collects round the extremity of the iron wire.

2. Magnesium may be prepared in much larger quantity by reducing magnesium chloride, or the double chloride of magnesium and sodium or potassium, with metallic sodium. The double chloride is prepared by dissolving magnesium carbonate in hydrochloric acid, adding an equivalent quantity of sodium or potassium chloride, evaporating to dryness, and fusing the residue. This product, heated with sodium in a wrought-iron crucible, yields metallic magnesium, containing certain impurities, from which it may be freed by distillation. This process is now carried out on the manufacturing scale, and the magnesium is drawn out into wire or formed into riband for burning.

Magnesium is a brilliant metal, almost as white as silver, somewhat more brittle at common temperatures, but malleable at a temperature a little below redness. Its density is 1·75. It melts at a red heat, and volatilises at nearly the same temperature as zinc. It retains its lustre in dry air, but in moist air it becomes covered with a crust of magnesia.

Magnesium in the form of wire or riband takes fire at a red heat, burning with a dazzling bluish-white light. The flame of a candle or spirit-lamp is sufficient to inflame it, but to insure continuous combustion, the metal must be kept in contact with the flame. For this purpose lamps have been constructed, provided with a mechanism which continually pushes three or more magnesium wires into a small spirit-flame.

The magnesium flame produces a continuous spectrum, containing a very large proportion of the more refrangible rays: hence it is well adapted for photography, and has, indeed, been used for taking photographs, in the absence of the sun, or in places where sunlight cannot penetrate, as in caves or subterranean apartments.

Magnesium Chloride, $MgCl_2$.—When magnesia, or its carbonate, is dissolved in hydrochloric acid, magnesium chloride and water are produced; but when this solution is evaporated to dryness, the last portions of water are retained with such obstinacy, that decomposition of the water is brought about by the concurring attractions of magnesium for oxygen, and of chlorine for hydrogen, hydrochloric acid being expelled, and magnesia remaining. If, however, sal-ammoniac, potassium chloride, or sodium chloride, is present, a double salt is produced, which is easily rendered anhydrous. The best mode of preparing the chloride is to divide a quantity of hydrochloric acid into two equal portions, to neutralise one with magnesia, and the other with ammonia, or carbonate of ammonia: to mix these solutions, evaporate them to dryness, and then expose the salt to a red heat in a loosely covered porcelain crucible. Sal-

ammoniac sublimes, and fused magnesium chloride remains: the latter is poured out upon a clean stone, and when cold transferred to a well-stopped bottle.

The chloride so obtained is white and crystalline. It is very deliquescent and highly soluble in water, from which it cannot again be recovered by evaporation, for the reasons just mentioned. When long exposed to the air in the melted state, it is converted into magnesia. It is soluble in alcohol.

Magnesium chloride occurs in sea-water, in many brine-springs and salt-beds, and is prepared in large quantities at Stassfurt.

Magnesium Oxide, or Magnesia, MgO, is easily prepared by exposing the *magnesia alba* of pharmacy, which is a hydrocarbonate, to a full red heat in an earthen or platinum crucible. It forms a soft, white powder, which slowly attracts moisture and carbonic acid from the air, and unites quietly with water to a slightly soluble hydrate requiring for solution about 5000 parts of water at 15·5° and 36,000 parts at 100°. The alkalinity of magnesia can be observed only by placing a small portion in the moist state upon test-paper; but it neutralises acids completely. It is infusible in the blow-pipe flame.

Experiment.—Take a strip of magnesium ribbon, six inches long, and holding it by tongs, ignite one end by a lighted match or gas flame. Let the resulting white oxide fall into a small clean porcelain dish. Wet it with distilled water and place in the mixture a piece of red litmus paper. The litmus slowly becomes blue.

Magnesium Sulphide is formed by passing vapour of carbon sulphide over magnesia at a strong red heat.

It is an earthy-looking substance, insoluble in and decomposed by water with evolution of sulphuretted hydrogen;

$$MgS + 2H_2O = Mg(HO)_2 + H_2S.$$

Magnesium Sulphate, $MgSO_4,7H_2O$, commonly called *Epsom salt*, occurs in sea-water, and in many mineral springs, and was formerly manufactured in large quantities by acting on magnesian limestone with dilute sulphuric acid, and separating the magnesium sulphate from the greater part of the slightly soluble calcium sulphate by filtration. It is, however, now chiefly manufactured from the mineral kieserite, $MgSO_4H_2O$, present in considerable quantity in certain portions of the salt deposits at Stassfurt. The crystals are derived from a right rhombic prism; they are soluble in an equal weight of water at 5·5°, and in a still smaller quantity at 100°. The salt has a nauseous bitter taste, and, like many other neutral salts, possesses purgative properties. When it is exposed to heat, 6 molecules of water readily pass off, the seventh being firmly retained. Magnesium sulphate forms with the sulphates of potassium and ammonium, beautiful double salts which contain 6 molecules of

crystallisation-water, their formula being $MgK_2(SO_4)_2,6H_2O$, and $Mg(NH_4)_2,(SO_4)_2,6H_2O$. These salts are isomorphous, and form monoclinic crystals.

Experiment.—Take a small lump of magnesite (native carbonate), powder it and dissolve in dilute sulphuric acid, applying a gentle heat and adding the acid in small quantities till effervescence ceases. Filter the solution and let it crystallise. If no crystals are formed, evaporate the liquid till reduced in bulk, and let it cool again. If a piece of chalk be treated in the same way it will effervesce, but the resulting sulphate is almost insoluble, and the solution therefore yields no crystals.

Magnesium Phosphate, $MgHPO_4,7H_2O$, separates in small colourless prismatic crystals when solutions of sodium phosphate and magnesium sulphate are mixed and left at rest for some time. It is soluble in about 1000 parts of cold water. Magnesium phosphate exists in the grain of the cereals, and can be detected in considerable quantity in beer.

Magnesium and Ammonium Phosphate, $Mg(NH_4),PO_4,6H_2O$.—When ammonia or its carbonate is mixed with a magnesium salt, and a soluble phosphate is added, a crystalline precipitate having the above composition subsides, immediately if the solutions are concentrated, and after some time if they are very dilute: in the latter case, the precipitation is promoted by stirring. This salt is slightly soluble in pure water, but nearly insoluble in saline and ammoniacal liquids. When heated, it gives off water and ammonia, and is converted into *magnesium pyrophosphate*, $Mg_2P_2O_7$:—

$$2Mg(NH_4)PO_4 = Mg_2P_2O_7 + H_2O + 2NH_3.$$

At a strong red heat it fuses to a white enamel-like mass. Magnesium and ammonium phosphate sometimes forms a urinary calculus, and occurs also in guano. In analysis, magnesium is usually separated from solution by bringing it into this state.

Magnesium Silicates.—The following natural compounds belong to this class: *Chrysolite*, $Mg_2SiO_4=2MgO,SiO_2$, a crystallised mineral, sometimes employed for ornamental purposes: a portion of the magnesia is commonly replaced by ferrous oxide, which communicates a green colour. *Meerchaum*, $2MgSiO_3,SiO_2=2MgO,3SiO_2$, is a soft sectile mineral, from which pipe-bowls are made. *Talc*, $4MgSiO_3,SiO_2,4H_2O$ (called *steatite* when massive), is a soft, white, sectile, transparent or translucent mineral, used in the state of powder for diminishing friction. *Soapstone*, also called steatite, is a silicate of magnesium and aluminium of somewhat variable composition. *Serpentine* is a combination of silicate and hydroxide of magnesium. *Jade*, an exceedingly hard stone, brought from China and from New Zealand, is a silicate of magnesium and aluminium: its green colour is due to chromium. *Augite* and *hornblende* are essentially

double silicates of magnesia and lime, in which the magnesia is more or less replaced by its isomorphous substitute, ferrous oxide.

Magnesium Carbonates.—The *Normal Carbonate*, $MgCO_3$ or MgO,CO_2, occurs native in rhombohedral crystals, resembling those of calc-spar, imbedded in talc-slate : a soft earthy variety is sometimes met with.

When magnesia alba is dissolved in aqueous carbonic acid, and the solution left to evaporate spontaneously, small prismatic crystals are deposited, consisting of trihydrated magnesium carbonate, $MgCO_3 3H_2O$.

The magnesia alba itself, although often called carbonate of magnesium, is not so in reality ; it is a compound of carbonate with hydroxide. It is prepared by mixing hot solutions of potassium or sodium carbonate and magnesium sulphate, the latter being kept in slight excess, boiling the whole for a few minutes. during which time much carbonic acid is disengaged, and well washing the precipitate so produced. If the solution is very dilute, the magnesia alba is exceedingly light and bulky; if otherwise, it is denser. The composition of this precipitate is not perfectly constant. In most cases it contains $3MgCO_3,MgH_2O_2,4H_2O$.

Magnesia alba is slightly soluble in water, especially when cold.

Experiments.—1. Dissolve about 2 ounces of Epsom salt and an equal quantity of crystals of soda, each in a quarter of a pint of water. Mix the solution in a dish, evaporate the mixture rapidly with constant stirring till the residue is quite dry. Then boil what remains with water, and collect the precipitate (carbonate of magnesium) on a clean calico filter, pour hot water over it once or twice, drain and squeeze it, and place the filter in an oven to dry.

2. Heat a portion of the dry powder to redness in a porcelain crucible. Let it cool, and test it for carbonate by dissolving a little in an acid. It is magnesium oxide, and should not effervesce.

3. Dissolve the rest of the oxide in dilute sulphuric acid, crystallise the salt, and compare the crystals with those made from magnesite.

Magnesium salts are isomorphous with zinc salts, ferrous salts, cupric salts, cobalt salts, and nickel salts, etc. ; they are usually colourless, and are easily recognised by the following characters :—A solution in water gives a gelatinous white precipitate with *caustic alkalis*, including *ammonia*, insoluble in excess, but soluble in solution of sal-ammoniac : a white precipitate with *potassium* and *sodium carbonates*, but none with ammonium carbonate in the cold : a white crystalline precipitate with soluble *phosphates*, especially on the addition of a little ammonia.

Magnesium salts give no precipitate with hydrogen sulphide or ammonium sulphide, nor with solution of platinic chloride.

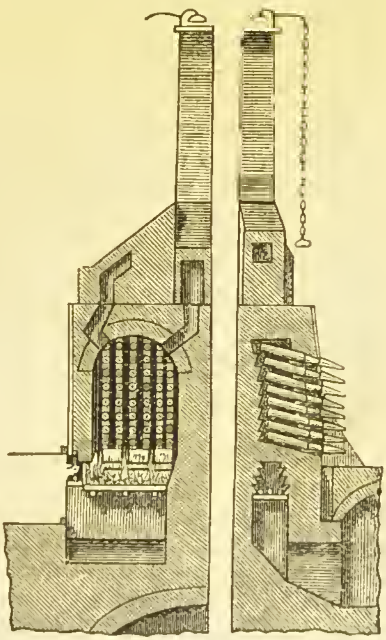
ZINC.

Symbol, Zn. Atomic weight, 65. Vapour density, 32·5.

It is not known by whom zinc was discovered, but writers of the sixteenth century described its properties. The ancients were not acquainted with zinc as a separate metal, but its ores were used in the manufacture of brass.

Zinc is a somewhat abundant metal: it is found in the state of carbonate, silicate, and sulphide, associated with lead ores in many districts, both in Britain and on the Continent; large supplies are obtained from Silesia, and from the neighbourhood of Aachen. The native carbonate, or *calamine*, is a valuable zinc ore, and is preferred for the extraction of the metal, but large quantities are made from *blende*, which is the sulphide, ZnS. It is first roasted to expel water and carbon dioxide, the oxide is then mixed with ground coal, and distilled at a full red heat in a large earthen retort: carbon monoxide then escapes, while the reduced metal volatilises and is condensed by suitable means.

Fig. 132.



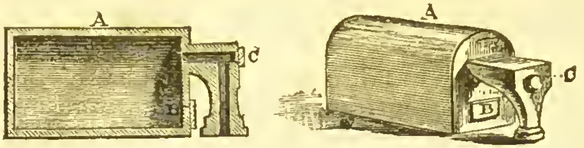
When blende, or 'black jack,' is employed, it also is submitted to a preliminary roasting in a current of air, whereby it is converted into the oxide:—

$$ZnS + 3O = ZnO + SO_2.$$

The form of apparatus employed varies in different districts. Fig. 132 represents the Belgian zinc furnace, which is used not only on the Continent but in this country. It consists of an arched chamber having the fire grate below, and in its upper part several rows of fireclay tubes or retorts, each about 4 feet long. Each of these is provided with a fireclay conical adapter and a receiver of sheet-iron, which projects from the side of the furnace, and in which the zinc as it distils away is collected. The figure on the right shows the position of the tubes in the furnace; on the left a front view of the same. The Silesian apparatus consists of a series of fireclay retorts in the form of a muffle, as shown in fig. 133. The retorts are arranged in two rows, back to back, with the fire between

them, so that the nozzles and condensing chambers are attached on opposite sides of the furnace. About 100 pounds weight of the mixture of ore and coal forms the charge for each muffle.

Fig. 133.



Zinc is a bluish-white metal, which slowly tarnishes in the air: it has a lamellar crystalline structure, a density varying from 6·8 to 7·8, and is under ordinary circumstances, brittle. Between 120° and 150°, it is, on the contrary, malleable, and may be rolled or hammered without danger of fracture; and, what is very remarkable, after such treatment, it retains its malleability when cold: the sheet-zinc of commerce is thus made. At 210° it is so brittle that it may be reduced to powder. It melts at 412°; boils at 1040° (Deville and Troost), and, if air be admitted, burns with a splendid greenish light, generating the oxide. Dilute acids dissolve zinc very readily: it is constantly employed in this manner for preparing hydrogen gas.

The application of metallic zinc to the purposes of roofing, the construction of water-channels, etc., are well known; it is sufficiently durable, but inferior in this respect to copper. *Galvanised iron* consists of iron having its surface coated with zinc.

Zinc Chloride, $ZnCl_2$, may be prepared by heating metallic zinc in chlorine: by distilling a mixture of zinc-filings and corrosive sublimate; or, more easily, by dissolving zinc in hydrochloric acid. It is a nearly white, translucent, fusible substance, very soluble in water and alcohol, and very deliquescent. A strong solution of zinc chloride is sometimes used as a bath for obtaining a graduated temperature above 100°. Zinc chloride unites with sal-ammoniac and potassium chloride to form double salts: the former of these, made by dissolving zinc in hydrochloric acid, and then adding an equivalent quantity of sal-ammoniac, is very useful in tinning and soft-soldering copper and iron.

Zinc Oxide, ZnO, is strongly basic, forming salts isomorphous with the magnesium salts. It is prepared either by burning zinc in atmospheric air, or by heating the carbonate to redness. Zinc oxide is a white, tasteless powder, insoluble in water, but freely dissolved by acids. When heated it is yellow, but turns white again on cooling. It is sometimes used as a substitute for white lead. To prepare zinc-white on a large scale, metallic zinc is volatilised in large earthen muffles, whence the zinc vapour passes into a small receiver (*guérite*), where it comes in contact with a current of air and is oxidised. The zinc oxide thus formed passes immediately into a condensing chamber, divided into several compartments by cloths suspended within it.

Oxysalts of Zinc.—The *Sulphate*, $ZnSO_4,7H_2O$, commonly called *White Vitriol*, is hardly to be distinguished by the eye from magnesium sulphate : it is prepared either by dissolving the metal in dilute sulphuric acid, or, more economically, by roasting the native sulphide, or *blende*, which, by absorption of oxygen, becomes in great part converted into sulphate. The altered mineral is thrown hot into water, and the salt is obtained by evaporating the clear solution. Zinc sulphate has an astringent metallic taste, and is used in medicine as an emetic. The crystals dissolve in $2\frac{1}{2}$ parts of cold, and in a much smaller quantity of hot water. Crystals containing 6 molecules of water have been observed. Zinc sulphate forms double salts with the sulphates of potassium and ammonium, namely, $ZnK_2(SO_4)_2,6H_2O$ and $Zn(NH_4)_2,(SO_4)_2 6H_2O$, isomorphous with the corresponding magnesium salts.

Experiment.—Dissolve an ounce of granulated zinc in diluted sulphuric acid in a beaker or evaporating dish. Filter, if necessary, from any undissolved flakes of lead, and let the liquid cool, with a view to the production of crystals. If none form after a few hours, evaporate away a portion of the water, and set aside the solution again. If the liquid be allowed to crystallise slowly, crystals of considerable size may form, which should be compared with crystals produced by similar slow deposition from a solution of magnesium sulphate.

The *Carbonate*, $ZnCO_3$ is found native ; the white precipitate obtained by mixing solutions of zinc and of alkaline carbonates, is a combination of carbonate and hydroxide, $ZnCO_3,Zn(HO)_2,2H_2O$.

When heated to redness, it yields pure zinc oxide.

Experiment.—Substituting zinc sulphate for magnesium sulphate, prepare specimens of zinc carbonate and oxide.

Zinc Sulphide, ZnS, occurs native, as *blende*, in regular tetrahedrons, dodecahedrons, and other monometric forms, and of various colours, from white or yellow to brown or black, according to its degree of purity : it is a valuable ore of zinc. A variety, called *Black Jack*, occurs somewhat abundantly in Derbyshire, Cumberland, and Cornwall. A *hydrated sulphide*, ZnS,H_2O, is obtained as a white precipitate on adding an alkaline sulphide to the solution of a zinc salt.

Zinc salts are distinguished by the following characters :—*Caustic potash*, *soda*, and *ammonia* give a white precipitate of hydroxide, freely soluble in excess of the alkali. *Potassium* and *sodium carbonates* give white precipitates, insoluble in excess. *Ammonium carbonate* gives also a white precipitate, which is redissolved by an excess. *Potassium ferrocyanide* gives a white precipitate. *Hydrogen sulphide* causes no change in zinc solutions containing free mineral acids ; but in neutral solutions, or with zinc salts of organic acids, such as the acetate, a white precipitate is formed. *Ammonium sulphide* throws down white sulphide of zinc, insoluble in caustic alkalis. The formation of this precipitate in a solution containing excess of caustic alkali, serves to distinguish zinc from all other metals.

All zinc compounds, heated on charcoal with sodium carbonate in the inner blow-pipe flame, give an incrustation of zinc oxide, which is yellow while hot, but becomes white on cooling. If this incrustation be moistened with a dilute solution of cobalt nitrate, and strongly heated in the outer flame, a fine green colour is produced.

CADMIUM.

Symbol, Cd. Atomic weight, 112. Vapour density, 56.

This metal was discovered in 1817 by Stromeyer, and by Hermann: it accompanies the ores of zinc, especially those occurring in Silesia, and, being more volatile than that substance, rises first in vapour when the calamine is subjected to distillation with coal. From these portions of the metal cadmium can be extracted by dissolving in hydrochloric acid, and precipitating the acid solution with sulphuretted hydrogen, which throws down the cadmium in the form of a yellow sulphide. The sulphide is then filtered off, washed, roasted into oxide, and distilled with charcoal. Cadmium resembles tin in colour, but is somewhat harder; it is very malleable, has the density 8·7, melts below 260°, and is nearly as volatile as mercury. It tarnishes but little in the air, but burns when strongly heated. Dilute sulphuric and hydrochloric acids act but little on cadmium in the cold; nitric acid is its best solvent.

The observed vapour-density of cadmium is 3·94 compared with air, or 56·3 compared with hydrogen, which latter number does not differ greatly from the half of 112, the atomic weight of the metal: hence it appears that, as in the case of the allied metals zinc and mercury, the molecule is monatomic (p. 243).

Cadmium Oxide, CdO, may be prepared by igniting either the carbonate or the nitrate: in the former case it has a pale-brown colour, and in the latter a much darker tint, and forms octahedral microscopic crystals. Cadmium oxide is infusible: it dissolves in acids, producing a series of colourless salts: it absorbs carbon dioxide from the air, and turns white. The *sulphate* is easily obtained by dissolving the oxide or carbonate in dilute sulphuric acid: it is very soluble in water. It usually has the composition $3CdSO_4,8H_2O$, but it behaves like the sulphates of zinc and magnesium in forming double salts with the sulphates of potassium and ammonium, which contain respectively $CdK_2(SO_4)_2,6H_2O$ and $Cd(NH_4)_2(SO_4)_2,6H_2O$. The *chloride*, $CdCl_2$, is a very soluble salt, crystallising in small four-sided prisms. The *sulphide*, CdS, is a very characteristic compound, of a bright yellow colour, forming microscopic crystals, fusible at a high temperature. It is obtained by passing sulphuretted hydrogen gas through a solution of the sulphate, nitrate, or chloride. This compound is used as a yellow pigment, of great beauty and permanence. It occurs native as the rare mineral *Greenockite*.

Fixed caustic *alkalis* give with cadmium salts a white precipitate of hydroxide, insolnble in excess. *Ammonia* gives a similar white precipitate, readily soluble in excess. The *fixed alkaline carbonates*, and *ammonia carbonate*, throw down white cadmium carbonate, insoluble in excess of either precipitant. *Hydrogen sulphide* and *ammonium sulphide* precipitate the yellow sulphide of cadmium, which, unlike zinc sulphide, is precipitated in the presence of dilute mineral acids, such as hydrochloric and sulphuric acids. It is decomposed by boiling with dilute sulphuric acid.

MERCURY.

Symbol, Hg (Hydrargyrum). Atomic weight, 200. Vapour-density, 100.

This very remarkable metal, sometimes called *quicksilver*, has been known from early times, and perhaps more than all others has excited the attention and curiosity of experimenters, by reason of its peculiar physical properties. Mercury is of great importance in several of the arts, and enters into the composition of many valuable medicines.

Metallic mercury is occasionally met with in globules disseminated through the native sulphide, which is the ordinary ore. This latter substance, sometimes called *cinnabar*, is found in considerable quantity in several localities, of which the most celebrated are Almaden in Spain, and Idria in Austria. It has also been discovered in great abundance, and of remarkable purity, in California and Australia.

The metal is obtained by heating the sulphide in an iron retort with lime or scraps of iron, or by roasting it in a furnace, and conducting the vapours into a large chamber, where the mercury is condensed, while the sulphurous oxide is allowed to escape. Mercury is imported into this country in bottles of hammered iron, containing about seventy-five pounds each, and in a state of considerable purity. When purchased in smaller quantities, it is sometimes found adulterated with tin and lead, which metals it dissolves to some extent without much loss of fluidity. Such admixture may be known by the foul surface which the mercury exhibits when shaken in a bottle containing air, and by the globules, when made to roll upon the table, leaving a train or tail. Mercury may be partly purified by agitation with a small quantity of nitric acid, which attacks the foreign metals first, and afterwards washing with water. It can be obtained pure by distilling below its boiling point under reduced pressure.

Mercury has a nearly silver-white colour, and a very high degree of lustre: it is liquid at all ordinary temperatures, and solidifies only when cooled to $-39°$. In this state it is soft and malleable.

It boils at 357·25° (Regnault), yielding a transparent, colourless vapour, of great density. The metal volatilises, however, to a sensible extent at all temperatures above 19° or 21°; below this point its volatility is imperceptible. The volatility of mercury at the boiling temperature is much retarded by the presence of minute quantities of lead or zinc. The density of mercury at 15·5° is 13·59; that of frozen mercury about 14, great contraction taking place in the act of solidification.

Pure mercury is quite unalterable in the air at common temperatures, but when heated to near its boiling point, it slowly absorbs oxygen, and becomes converted into a crystalline dark-red powder, which is the highest oxide. At a dull red heat this oxide is again decomposed into its constituents. Hydrochloric acid has little or no action on mercury, and the same may be said of sulphuric acid in a diluted state: but when the acid is concentrated and boiling hot, it converts the metal into mercuric sulphate, with evolution of sulphur dioxide, $Hg + 2H_2SO_4 = HgSO_4 + H_2O + SO_2$. Nitric acid, even dilute and in the cold, dissolves mercury freely, with evolution of nitric oxide and formation of mercurous or mercuric nitrate according to the relative proportions of the metal and acid.

The observed vapour-density of mercury referred to air as unity is 6·7; this referred to hydrogen is nearly 100;* that is to say, half the atomic weight of the metal: consequently the atom of mercury, like that of zinc and cadmium, occupies in the gaseous state twice the volume of an atom of hydrogen (see p. 243).

Alloys of mercury with other metals are termed *amalgams*: mercury dissolves in this manner many of the metals, as gold, silver, tin, lead, etc. These combinations sometimes take place with considerable violence, as in the case of potassium, in which light and heat are produced; besides this, many of the amalgams after a while become solid and crystalline. The amalgam of tin used in silvering looking-glasses, and that of silver and of copper, sometimes employed for stopping hollow teeth, are examples. The solid amalgams appear to be, for the most part, definite compounds, while the liquid amalgams may be regarded, in many instances, as mixtures of definite compounds with excess of mercury, inasmuch as, when they are pressed between chamois leather, mercury, containing only a small quantity of the other metal, passes through, while a solid amalgam, frequently of definite atomic constitution, remains behind. A native compound of mercury and silver, called "amalgam" by mineralogists, and having the composition Ag_2Hg_2, or Ag_2Hg_3, is found crystallised in octahedrons, rhombic dodecahedrons, and other forms of the regular system.

Mercury forms two series of compounds, namely, the mercuric compounds, as $HgCl_2$, HgO, $HgSO_4$, etc., and the mercurous compounds, Hg_2Cl_2, Hg_2O, etc. These compounds are analogous in constitution to the cupric and cuprous compounds; and the mercurous compounds, like the latter, are easily converted into mercuric compounds by the action of oxidising agents, which remove one atom

of mercury ; but they are, on the whole, much more stable than the cuprous compounds.

Mercury Chlorides.—*Mercuric Chloride*, $HgCl_2$, commonly called *Corrosive Sublimate.*—This compound may be obtained by several different processes ; (1) When metallic mercury is heated in chlorine gas, it takes fire and burns, producing this substance. (2) It may be made by dissolving mercuric oxide in hot hydrochloric acid, crystals of corrosive sublimate then separating on cooling. (3) Or, more economically, by subliming a mixture of equal parts of mercuric sulphate and dry common salt ; and this is the plan generally followed. The decomposition is represented by the equation :

$$HgSO_4 \quad + \quad 2NaCl \quad = \quad HgCl_2 \quad + \quad Na_2SO_4.$$

Sublimed mercuric chloride forms a white transparent crystalline mass, of density 5·43 ; it melts at 265°, boils at 295°, and volatilises somewhat more easily than calomel, even at ordinary temperatures. Its observed vapour-density, referred to hydrogen as unity, is 140 : and the density calculated from the formula $HgCl_2$, supposing that the molecule occupies the same space as a molecule or two atoms of hydrogen, is $\frac{200+2\times 35{\cdot}4}{2}=135{\cdot}4$; the near agreement of this number with the observed result shows that the vapour is in the normal state of condensation.

Mercuric chloride dissolves in 16 parts of cold and 3 parts of boiling water, and crystallises from a hot solution in long white prisms. Alcohol and ether also dissolve it easily ; the latter even withdraws it from a watery solution.

Mercuric chloride combines with a great number of other metallic chlorides, forming a series of beautiful double salts, of which the ancient *sal alembroth* may be taken as a good example : it contains $HgCl_2,2NH_4Cl,H_2O$. The chloride absorbs ammoniacal gas with great avidity, generating the compound $HgCl_2,NH_3$.

Mercuric chloride forms several compounds with mercuric oxide. These are produced by several processes, as when an alkaline carbonate is added in varying proportions to a solution of mercuric chloride. They differ greatly in colour and physical character, and are mostly decomposed by water.

Mercuric chloride forms insoluble compounds with proteid substances, such as albumin. It is perhaps to this property that its strong antiseptic properties are due. Animal and vegetable substances are preserved by it from decay, as in Kyan's method of preserving timber and cordage. Albumin is on this account an excellent antidote to corrosive sublimate in cases of poisoning.

Mercurous Chloride, Hg_2Cl_2, commonly called *Calomel.* — This very important substance may be easily prepared by pouring a solution of mercurous nitrate into a large excess of dilute solution of common salt. It falls as a dense white precipitate, quite insoluble

in water ; it must be thoroughly washed with boiling distilled water, and dried. Calomel is, however, generally procured by another process. Dry mercuric sulphate is rubbed in a mortar with as much metallic mercury as it already contains, and a quantity of common salt, until the globules disappear, and a uniform mixture has been produced. This is subjected to sublimation, and the vapour of the calomel being carried into an atmosphere of steam, or into a chamber containing air, is thus condensed in a minutely divided state, and the laborious process of pulverisation of the sublimed mass is avoided. The reaction is thus explained :

$$HgSO_4 + Hg + 2NaCl = Hg_2Cl_2 + Na_2SO_4.$$

Pure calomel is a heavy white insoluble tasteless powder : it rises in vapour at a temperature below redness, and is obtained by ordinary sublimation as a yellowish-white crystalline mass. It is as insoluble in cold dilute nitric acid as silver chloride ; boiling-hot strong nitric acid oxidises and dissolves it. Calomel is instantly decomposed by an alkali, or by lime-water, with production of black mercurous oxide. After long keeping, especially if exposed to daylight, it is sometimes apt to contain a little mercuric chloride, which would be a very dangerous contamination in calomel employed for medical purposes. This is easily discovered by boiling with water, filtering the liquid, and adding caustic potash. Any corrosive sublimate is indicated by a yellow precipitate.

The observed vapour-density of calomel, referred to hydrogen as unity, is 119·2. Now the formula Hg_2Cl_2, if it represents a molecule occupying in the gaseous state two volumes (*i.e.*, twice the volume of an atom of hydrogen), would give a density nearly double of this : for $\frac{400+2.35{\cdot}4}{2} = 235{\cdot}4$. Hence it might be inferred that the composition of calomel should rather be represented by the simpler formula HgCl, which would give for the vapour-density the number 117·7. The frequent decomposition of mercurous salts into mercuric salts and free mercury tends however to favour the supposition that their molecules contain two atoms of mercury ; and the anomaly in the vapour-volume of calomel may be explained by supposing that the vapour of this compound, like that of many others, undergoes dissociation at high temperatures, the two volumes of mercurous chloride, Hg_2Cl_2, being resolved into two volumes of mercuric chloride, $HgCl_2$ and two volumes of mercury, Hg. This supposition has been, to some extent, supported by the observation that calomel vapour amalgamates gold leaf, and that corrosive sublimate may be detected in resublimed calomel.

Iodides.—*Mercuric Iodide*, HgI_2 is formed when solution of potassium iodide is mixed with mercuric chloride, as a precipitate which is at first yellow, but in a few moments changes to a most brilliant scarlet, this colour being retained on drying. This is the

normal iodide: it may be made, although of rather duller tint, by triturating equivalent quantities of iodine and mercury with a little alcohol. In preparing it by precipitation, it is better to weigh out the proper proportions of the two salts, as the iodide is soluble in an excess of either, more especially in excess of potassium iodide. Mercuric iodide exhibits a very remarkable case of dimorphism, attended with difference of colour, which is red or yellow, according to the figure assumed. Thus, when the iodide is suddenly exposed to a high temperature, it becomes bright yellow throughout, and yields a copious sublimate of minute but brilliant yellow crystals. If in this state it be touched by a hard body, it instantly becomes red, and the same change happens spontaneously after a certain lapse of time. On the other hand, by a very slow and careful heating, a sublimate of red crystals, having a totally different form, may be obtained, which are permanent. The same kind of change happens with the freshly precipitated iodide, the yellow crystals first formed breaking up in a few seconds, from the passage of the salt to the red modification.

Mercuric iodide forms double salts with the more basic or positive metallic iodides, as those of the alkali-metals and alkaline earth-metals; thus it dissolves in aqueous potassium iodide, and the hot solution deposits, on cooling, crystals, of potassio-mercuric iodide $2(KI,HgI_2),3H_2O$. They are decomposed by water, with separation of about half the mercuric iodide, the solution then containing the salt $2KI,HgI_2$, which remains as a saline mass on evaporation.

Mercurous Iodide, Hg_2I_2, is formed when a solution of potassium iodide is added to mercurous nitrate: it then separates as a dirty yellow insoluble precipitate, with a tinge of green. It may also be prepared by rubbing mercury and iodine together in a mortar in the proportion of 1 atom of the former to 1 atom of the latter, the mixture being moistened from time to time with alcohol.

Experiments.—1. Place in a mortar 5 grams of mercury and $6\frac{1}{2}$ grams of iodine, add a few drops of spirit of wine, and rub the elements together till complete combination has been accomplished. The red powder is mercuric iodide HgI_2. When quite dry, place it in a small dry beaker, into which a second beaker, containing a little cold water, will just slide. Support the inner beaker by means of a piece of paper, or otherwise, so that its bottom is about an inch above the iodide. Place the whole arrangement on a sand-bath, and apply gentle heat till the iodide has completely sublimed. Read the preceding description of the changes of colour which may be observed.

2. By using twice the quantity of mercury or half the quantity of iodine required in Experiment 1, and following the same method, the mercurous iodide may be obtained. It is partially decomposed by sublimation.

Oxides.—*Monoxide*, or *Mercuric Oxide*, HgO, commonly called *Red Oxide of Mercury*, or *Red Precipitate.*—There are numerous methods

by which this compound may be obtained. The following may be cited as the most important:—1. By exposing mercury in a glass flask with a long narrow neck, for several days, to a temperature approaching 315°. The product has a dark red colour, and is highly crystalline; it is the *mercurius calcinatus per se* or *red precipitate* of the old writers. 2. By cautiously heating any of the mercuric or mercurous nitrates to complete decomposition, whereby the acid radicle is decomposed and expelled, oxidising the metal to the maximum, if it happens to be in the state of mercurous salt. The product thus obtained is also crystalline and very dense, but has a much paler colour than the preceding; while hot, it is nearly black. It is by this method that the oxide is generally prepared: it is apt to contain undecomposed nitrate, which may be discovered by strongly heating a portion in a test-tube: if red fumes are produced, or the odour of nitric peroxide exhaled, the oxide has been insufficiently heated in the process of manufacture. 3. By adding caustic potash in excess to a solution of corrosive sublimate, by which a bright yellow precipitate of mercuric oxide is thrown down, which is destitute of crystalline texture and retains after drying a small quantity of water. It is converted into the red variety by strong heat.

Mercuric oxide is slightly soluble in water, communicating to the latter an alkaline reaction and metallic taste: it is highly poisonous. When strongly heated it is decomposed, as before observed, into metallic mercury and oxygen gas.

Mercurous Oxide, Hg_2O; *Suboxide*, or *Black Oxide of Mercury.*—This oxide is easily prepared by adding caustic potash to mercurous nitrate, or by digesting calomel in solution of caustic alkali. It is a dark grey, nearly black, heavy powder, insoluble in water, slowly decomposed by the action of light into metallic mercury and red oxide. The preparations known in pharmacy by the names of *blue pill*, *grey ointment*, *mercury with chalk*, etc., often supposed to owe their efficacy to this substance, merely contain the finely-divided metal.

Experiments.—1. Dissolve about 10 grams of mercury in nitric acid, and evaporate the solution to complete dryness; charge the dry yellow nitrate into a small dry flask, and place the flask over a rose burner in a fume-chamber. Apply heat till the mass becomes black, and on looking through the flask yellow vapour is no longer visible. The product when cold is red and crystalline.

2. Dissolve the oxide thus obtained in hydrochloric acid, diluted with three times its bulk of water. On cooling, white prisms of mercuric chloride are formed.

3. To a portion of the solution from Experiment 2 add excess of solution of potash. Yellow mercuric oxide is thrown down.

4. Shake up a few grams of mercurous chloride with solution of potash. Black mercurous oxide results. Filter it off, wash with hot water, and dry in a steam oven.

Mercury Nitrates and Nitrites.—Nitric acid varies in its action upon mercury according to the temperature. When cold and some-

what diluted, it forms only mercurous salts, and these are normal or basic—*i.e.*, oxynitrates (p. 318)—as the acid or the metal happens to be in excess. When, on the contrary, the nitric acid is concentrated and hot, a mercuric salt is produced. Both classes of salts are apt to be decomposed by a large quantity of water, giving rise to insoluble, or sparingly soluble, basic compounds.

Mercuric Nitrates.—By dissolving mercuric oxide in excess of nitric acid, and evaporating gently, a syrupy liquid is obtained, which, enclosed in a bell-jar over lime or sulphuric acid, deposits bulky crystals and crystalline crusts, both having the composition $2Hg(NO_3)_2,H_2O$. The same substance is deposited from the syrupy liquid as a crystalline powder by dropping it into concentrated nitric acid. The syrupy liquid itself appears to be a definite compound, containing $Hg(NO_3)_2,H_2O$. By saturating hot dilute nitric acid with mercuric oxide, a salt is obtained on cooling, which crystallises in needles permanent in the air, containing $Hg(NO_3)_2, HgO,H_2O$. The preceding crystallised salts are decomposed by water, with production of compounds more and more basic as the washing is prolonged, or the temperature of the water raised.

Mercurous Nitrate $(Hg_2)(NO_3)_2, 2H_2O$, forms large colourless crystals soluble in a small quantity of water without decomposition; it is made by dissolving mercury in an excess of cold dilute nitric acid. When excess of mercury has been employed, a finely crystallised basic salt is deposited after some time, containing $(Hg_2)(NO_3)_2, 2Hg_2O, 3H_2O$; in this is also decomposed by water. The two salts are easily distinguished when rubbed in a mortar with a little sodium chloride; the normal compound gives sodium nitrate and calomel; the basic salt, sodium nitrate and a black compound of calomel with mercurous oxide. A black substance, called *Hahnemann's soluble mercury*, is produced when ammonia in small quantity is dropped into a solution of mercurous nitrate: the composition of this preparation varies according to the temperature and the concentration of the solutions.

A yellow crystalline deposit is often formed in the preparation of mercurous nitrate by the action of cold dilute nitric acid upon mercury. This is said to consist of mercurous nitrite $Hg_2(NO_2)_2$.

Mercury Sulphates.—*Mercuric Sulphate*, $HgSO_4$, is readily prepared by boiling together oil of vitriol and metallic mercury until the latter is wholly converted into a heavy white crystalline powder, which is the salt in question; the excess of acid is then removed by evaporation carried to perfect dryness. Equal weights of acid and metal may be conveniently employed. Water decomposes the sulphate, dissolving out an acid salt, and leaving an insoluble, yellow, basic compound, formerly called *turpith* or *turbeth mineral*, $3HgSO_4 + 2H_2O = Hg_3SO_4O_2 + 2H_2SO_4$.

This compound may be regarded as a derivative of *ortho*-sulphuric acid H_6SO_6, or $(HO)_6S$. Long-continued washing with hot water entirely removes the acid radicle, and leaves pure mercuric oxide.

Mercurous Sulphate, Hg_2SO_4, falls as a white crystalline powder when sulphuric acid is added to a solution of mercurous nitrate : it is but slightly soluble in water and is decomposed thereby.

Mercury Sulphides.—*Mercuric Sulphide*, HgS, occurs native as *cinnabar*, a dull red mineral, which is the most important ore of mercury. Hydrogen sulphide passed in small quantity into a solution of mercuric nitrate, or chloride, forms a white precipitate, which is a compound of mercuric sulphide with the salt itself. An excess of the gas converts the whole into sulphide, the colour at the same time changing to black. When this black sulphide is sublimed, it becomes dark red and crystalline, but undergoes no change of composition: it is then *cinnabar* or *vermilion*. Mercuric sulphide is most easily prepared by subliming an intimate mixture of 6 parts of mercury and 1 part of sulphur, and reducing the resulting cinnabar to very fine powder, the beauty of the tint depending much upon the extent to which division is carried. The red or crystalline sulphide may also be formed directly, without sublimation, by heating the black precipitated substance in a solution of potassium pentasulphide. Mercuric sulphide is soluble to a certain extent in the alkaline sulphides, and forms with them crystallisable compounds.

When vermilion is heated in the air, it yields metallic mercury and sulphurous oxide : it resists the action both of caustic alkalis in solution, and of strong mineral acids, even nitric, and is attacked only by nitro-muriatic acid.

Mercurous Sulphide, Hg_2S, is obtained by passing hydrogen sulphide into a solution of mercurous nitrate, as a black precipitate, which is resolved at a gentle heat into mercuric sulphide and metallic mercury.

Ammoniacal Mercury Compounds.—By the action of ammonia and its salts on mercury compounds, a variety of substances are formed, which may be regarded as salts of mercurammoniums—that is, of ammonium-molecules in which the hydrogen is more or less replaced by mercury, or they may be viewed as mercury salts in which part of the acid radicle is replaced by the amidogen group NH_2. White precipitate, for example, may be represented by either of the following formulæ :—

$$\mathrm{Cl.N}\left\{\begin{array}{l}\mathrm{H_2}\\ \mathrm{Hg''}\end{array}\right. \qquad \mathrm{Cl-Hg-NH_2}$$

The following are the most important of these compounds.

Mercuric Compounds. — *Mercuro-diammonium Chloride*, $(N_2H_6Hg'')Cl_2$, known in pharmacy as *fusible white precipitate*, is produced by adding potash to a solution of ammonio-mercuric chloride, $(2NH_4Cl, HgCl_2)$, or by dropping solution of mercuric chloride into a boiling solution of sal-ammoniac containing free ammonia, as long as

the resulting precipitate redissolves: it then separates on cooling in regular dodecahedrons. At a gentle heat it gives off ammonia, leaving a chloride of mercurammonium and hydrogen, $(NH_2Hg'')Cl, HCl$:

$$N_2H_6Hg''Cl_2 = NH_3Hg''Cl_2 + NH_3.$$

Mercurammonium Chloride, $(NH_2Hg'')Cl$.—This salt, known in pharmacy as *infusible white precipitate*, is formed by adding ammonia to a solution of mercuric chloride. When first produced, it is bulky and white, but by contact with hot water, or by much washing with cold water, it is converted into hydrated dimercurammonium chloride NHg''_2Cl,H_2O.

Trimercuro-diammonium Nitrate, $(N_2H_2Hg''_3)(NO_3)_2 2H_2O$, is formed as a white precipitate, on mixing a dilute and very acid solution of mercuric nitrate with very dilute ammonia.

Trimercuro-diamine, $N_2Hg''_3$, a compound derived from a double molecule of ammonia N_2H_6, by substitution of 3 atoms of bivalent mercury for 6 atoms of hydrogen, is formed by passing dry ammonia gas over dry precipitated mercuric oxide:

$$3HgO + 2NH_3 = N_2Hg_3 + 3H_2O.$$

The excess of oxide being removed by nitric acid, the trimercuro-diamine is obtained as a dark-brown powder, which explodes by heat, friction, percussion, or contact with oil of vitriol, almost as violently as nitrogen chloride.

Dimercurammonium Chloride, NHg''_2Cl,H_2O, is obtained as already observed, by boiling mercurodiammonium chloride (infusible white precipitate) with water. It is a heavy, granular, yellow powder, which turns white again when treated with sal-ammoniac.

Dimercurammonium Iodide, NHg''_2I,H_2O.—This compound may be formed by digesting the corresponding chloride in a solution of potassium iodide; or by heating mercuric iodide with excess of aqueous ammonia:

$$2HgI_2 + 4NH_3 + H_2O = NHg''_2I,H_2O + 3NH_4I;$$

also by passing ammonia gas over mercuric oxy-iodide:

$$Hg_4I_2O_3 + 2NH_3 = 2(NHg''_2I,H_2O) + H_2O;$$

and, lastly, by adding ammonia to a solution of potassio-mercuric iodide mixed with caustic potash:

$$2(2KI,HgI_2) + 3KHO + NH_3 = NHg''_2I,H_2O + 7KI + 2H_2O.$$

This last reaction affords an extremely delicate test for ammonia. A solution of potassio-mercuric iodide is prepared by adding potassium iodide to a solution of corrosive sublimate, till a portion only of the resulting red precipitate is redissolved, then filtering, and mixing the filtrate with caustic potash. The liquid thus obtained forms, with a very small quantity of ammonia, either free or in the

form of an ammoniacal salt, a brown precipitate, soluble in excess of potassium iodide. This is called Nessler's test for ammonia.

Dimercurammonium Hydroxide, $NHg''_2(HO)$.—This compound is formed by treating precipitated mercuric oxide with aqueous ammonia, or by treating either of the dimercurammonium salts with a caustic alkali. It is a brown powder, which dissolves in acids, yielding salts of dimercurammonium.

Dimercurammonium Sulphate, $(NHg''_2)_2SO_4,2H_2O$, formerly called *ammoniacal turpethum*, is prepared by dissolving mercuric sulphate in ammonia, and precipitating the solution with water. It is a heavy white powder, yellowish when dry, resolved by heat into water, nitrogen, ammonia, and mercurous sulphate.

Mercurous Compounds. — *Mercurosammonium Chloride*, $(NH_3Hg''Cl)_2$, is the black precipitate formed when dry calomel is exposed to the action of ammonia gas. When exposed to the air, it gives off ammonia and leaves white mercurous chloride.—*Dimercurosammonium Chloride*, $NH_2Hg''_2Cl$, is formed, together with sal-ammonaic, by digesting calomel in aqueous ammonia:

$$Hg_2Cl_2 + 2NH_3 = NH_2Hg_2Cl + NH_4Cl.$$

It is grey when dry, and is not altered by boiling water.

Dimercurosammonium Nitrate, $2(NH_2Hg_2NO_3)H_2O$. This is supposed to be the composition of the velvet-black precipitate known as Hahnemann's soluble mercury, which is produced on adding ammonia to a solution of mercurous nitrate.

Reactions of Mercury Salts.—All mercury compounds are volatilised or decomposed by a temperature of ignition: those which fail to yield the metal by simple heating may in all cases be made to do so by heating in a test-tube with a little dry sodium carbonate. The metal is precipitated from its soluble combinations by metallic *copper*, also by a solution of *stannous chloride* used in excess.

Hydrogen sulphide and *ammonium sulphide* produce in solutions both of mercuric and of mercurous salts, black precipitates insoluble in ammonium sulphide. In mercuric salts, however, if the quantity of the reagent added is not sufficient for complete decomposition, a white precipitate is formed, consisting of a compound of mercuric sulphide with the original salt, and often coloured yellow or brown by excess of mercuric sulphide. An excess of hydrogen sulphide, or ammonium sulphide, instantly turns the precipitate black. This reaction is quite characteristic of mercuric salts.

Mercuric salts are further distinguished by forming a yellow precipitate with caustic *potash* or *soda*: white with *ammonia* or *ammonium carbonate*, insoluble in excess; red brown with *potassium* or *sodium carbonate*. With *potassium iodide* they yield a bright

scarlet precipitate, soluble in excess, either of the mercuric salt or of the alkaline iodide.

Mercurous salts are especially characterised by forming, with *hydrochloric acid* or *soluble chlorides*, a white precipitate which is turned black by ammonia. They also yield black precipitates with *caustic alkalis*; white with *alkaline carbonates*, soon turning black; greenish-yellow with *potassium iodide*.

METALS OF THE LEAD GROUP.

Lead—Thallium.

THESE metals are soft, heavy, and form oxides having a strongly alkaline reaction. Many of the compounds of thallium closely resemble the corresponding compounds of the alkali-metals. Thus it forms a soluble alkaline oxide and hydroxide and its sulphate is soluble and isomorphous with potassium sulphate, uniting in the same manner with aluminum sulphate to form an alum. The metal however resembles lead in density and other physical properties.

Many of the compounds of lead on the other hand are isomorphous with barium compounds, the nitrates and sulphates, for example, having the same crystalline form and similar properties as to density and solubility.

Lead and thallium are distinguished from both the alkalis and alkaline earths by the black colour and insolubility of their sulphides, and the sparing solubility of their dichlorides.

The relations of lead and thallium to these two groups are indicated in the list given below, from which it is obvious that thallium stands towards the alkali-metals in a position analogous to that of lead in regard to the alkaline earths.

	At. Wt.		At. Wt.
Lead	207	Thallium	204
Barium	137	Cæsium	133
Strontium	87·3	Rubidium	85
Calcium	40	Potassium	39

LEAD.

Symbol Pb (Plumbum). Atomic weight, 207.

Lead has been known from very early times. Remains of lead workings show that it was smelted in this country by the Romans before the Christian era.

This abundant and useful metal is wholly obtained from the native sulphide, or *galena*, no other lead-ore being found in large quantity. The reduction is effected in a reverberatory furnace, into which the crushed lead-ore is introduced and roasted for some time at a dull red heat, by which some of the sulphide is oxidised to oxide and some to sulphate. The contents of the furnace are then thoroughly mixed, and the temperature raised, whereupon the sulphate and

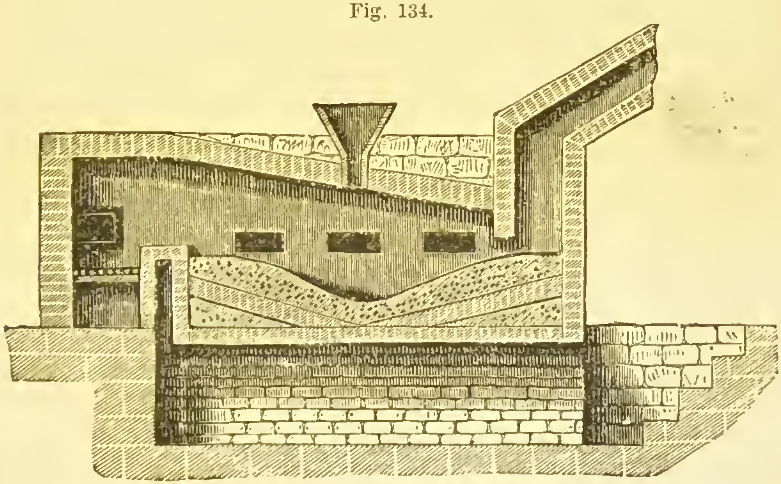
oxide react with the remaining sulphide in such a manner as to produce sulphur dioxide and metallic lead :—

$$2PbO + PbS = SO_2 + 3Pb$$
$$\text{and } PbSO_4 + PbS = 2SO_2 + 2Pb.$$

The furnace in which these operations are conducted is of the reverberatory type, as shown in fig. 134. The bed of the furnace is formed of lead slags, and there is a depression or well in the middle into which the lead runs as it is reduced. When the charge is worked out, the fluid metal is run off into an iron pot outside, from which, after stirring and skimming, it can be cast into pigs.

The lead thus produced sometimes contains antimony and other metals, which render it hard. They may, however, be removed and the lead rendered soft by melting and partially oxidising it in a reverberatory furnace with a cast-iron bottom. The lead so far

Fig. 134.



purified still contains silver in sufficient quantity to render it worth extracting; in fact, a considerable proportion of the silver which now comes into the market is obtained from argentiferous galena. The method of separating the silver will be described under "Silver."

Lead is a soft bluish metal, possessing very little elasticity; its density is 11·45. It may be easily rolled out into plates, or drawn out into coarse wires, but has very little tenacity. It melts at 327°, and boils and volatilises at a white heat. By slow cooling, it may be obtained in octahedral crystals. In moist air it becomes coated with a film of grey matter, thought to be sub-oxide, and when exposed to the atmosphere in the melted state it rapidly absorbs oxygen. Dilute acids, with the exception of nitric acid, act but slowly upon lead.

An alloy of 2 parts of lead and 1 of tin constitutes *plumber's*

solder; these proportions reversed give a more fusible compound, called *fine solder.* The lead employed in the manufacture of shot is combined with a little arsenic. *Type metal* consists of lead hardened by the addition of antimony and sometimes tin. *Pewter* contains about 1 part of lead to 4 parts of tin. A small quantity of lead, about 1 per cent., is added to brass which is intended for rolling.

Lead is a tetrad, as shown by the composition of plumbic ethide, $Pb(C_2H_5)_4$, and of the perchloride, $PbCl_4$, the peracetate $Pb(C_2H_3O_2)_4$ and the peroxide PbO_2. In the greater number of its compounds, however, it is bivalent, as in the dichloride, $PbCl_2$, the corresponding bromide and iodide, and the monoxide PbO.

Chlorides.—The *Dichloride*, $PbCl_2$, is prepared by precipitating a solution of lead nitrate or acetate with hydrochloric acid or common salt, and separates as a heavy white crystalline precipitate, which dissolves in about 33 parts of boiling water, and separates again, on cooling, in needle-shaped crystals.

The *Perchloride*, probably $PbCl_4$, is obtained by dissolving the dioxide in strong well-cooled hydrochloric acid, whereby a yellow, strongly oxidising solution is obtained, from which water and alkalis throw down the dioxide.

Oxychlorides.—The compound $Pb_3Cl_2O_2$ or $PbCl_2,2PbO$ occurs crystallised in rhombic prisms on the Mendip Hills, and is thence called *Mendipite.* Another oxychloride, constituting Pattinson's white oxychloride, Pb_2Cl_2O or $PbCl_2,PbO$, is prepared for use as a pigment by grinding galena with strong hydrochloric acid, dissolving the resulting chloride in hot water, and precipitating with lime-water. A third oxychloride, $PbCl_2,7PbO$, called *Patent yellow* or *Turner's yellow*, is prepared by heating 1 part of sal-ammoniac with 13 parts of litharge.

Lead Iodide, PbI_2, is precipitated, on mixing the nitrate or acetate with potassium iodide, as a bright yellow powder, which dissolves in boiling water, and crystallises therefrom in beautiful yellow iridescent spangles.

Oxides.—*Diplumbic Oxide*, or *Lead Suboxide*, Pb_2O, is formed when the oxalate is heated in a closed vessel: a grey pulverulent substance is then left, which is resolved by acids into monoxide and metal. It absorbs oxygen with great rapidity when heated, and even when simply moistened with water and exposed to the air.

The *Monoxide*, PbO, called *Litharge* or *Massicot*, is the product of the direct oxidation of the metal. It is most conveniently prepared by heating the carbonate to dull redness; common *litharge* is impure monoxide which has undergone fusion. Lead oxide has a delicate straw-yellow colour, is very heavy, and slightly soluble in water, giving an alkaline liquid. It is soluble in potash, and crystallises from the solution in rhombic prisms. At a red heat it melts, and tends to crystallise on cooling. In the melted state it attacks and

dissolves siliceous matter with astonishing facility, often penetrating an earthen crucible in a few minutes. It is easily reduced when heated with organic substances of any kind containing carbon or hydrogen. It forms a large class of salts, often called *plumbic salts*, which are colourless if the acid itself is not coloured.

A *Hydroxide*, $Pb_2O(OH)_2$ or HOPb.O.Pb.OH, is obtained as a white precipitate by the action of air and water free from carbonic acid on metallic lead, and is thrown down as a white precipitate on addition of ammonia or a fixed alkali to a lead salt, the precipitate in the latter case being redissolved by excess of the reagent. The hydroxide gives off part of its water at 130°, and the whole at 145°. Both the hydroxide and the oxide are somewhat soluble in water, and turn reddened litmus paper blue.

The *Sesquioxide*, Pb_2O_3, is formed by the action of sodium hypochlorite on a solution of the monoxide in potash, and when a solution of red lead in acetic acid is precipitated by very dilute ammonia. The reddish-yellow powder thus formed contains water, part of which it retains even at 150°. It is resolved by acids into PbO and PbO_2.

Triplumbic Tetroxide, or *Red Lead*, is not of very constant composition, but generally contains Pb_3O_4 or $2PbO,PbO_2$. It is prepared by exposing the monoxide, which has not been fused, for a long time to the air, at a very faint red heat. It is a brilliant red and extremely heavy powder, decomposed, with evolution of oxygen, by a strong heat, and converted by acids into a mixture of monoxide and dioxide. It is used as a cheap substitute for vermilion.

The *Dioxide*, PbO_2, often called *Puce* or *Brown Lead-oxide*, is easily obtained by digesting red lead in dilute nitric acid, whereby lead nitrate is dissolved out, and insoluble dioxide left behind in the form of a deep-brown powder. It is also formed by the action of chlorine on lead salts in presence of alkalis, and by the electrolysis of lead salts, being deposited on the anode. The dioxide is decomposed by a red heat yielding up one-half of its oxygen. By hydrochloric acid at common temperatures it is converted into lead chloride, with disengagement of chlorine, and by hot sulphuric acid into sulphate, with liberation of oxygen.

Lead dioxide dissolves in warm undiluted acetic acid, and the solution on cooling yields thin, colourless, prismatic crystals of a definite tetracetate, $Pb(C_2H_3O_2)_4$. This compound may also be obtained from red-lead. It is decomposed by water with precipitation of the dioxide. On the other hand lead dioxide, when fused with excess of potassium hydroxide, yields crystalline *potassium plumbate*, $K_2PbO_32H_2O$, the solution of which gives, with most metallic salts, precipitates of the corresponding plumbates.

The dioxide is very useful in separating sulphurous oxide from gaseous mixtures, lead sulphate being then produced : $PbO_2+SO_2=PbSO_4$.

Experiment.—1. Weigh as exactly as possible 10 grams of sheet-lead in a small fireclay or porcelain dish. An assayer's roasting dish

is best. Place it over a Bunsen flame, heat till the lead is melted, then stir frequently with an iron wire. The lead speedily becomes encrusted with oxide, but its complete conversion into this compound will occupy some hours. The dish or crucible must not be heated to such a temperature as to melt the oxide. When finished weigh the product. 207 grams of lead should give 223 grams of PbO.

2. Mix carefully in a mortar 22½ grams of litharge with about 2 grams of charcoal powder. Place the whole of the mixture in a small crucible ; heat strongly but not to redness, stir round with an iron wire, then holding the crucible by tongs tap it gently so as to cause all the lead to settle to the bottom. Let it cool, extract the button of lead and weigh it. It should weigh about 20½ grams. $PbO = 223$ gives $Pb = 207$.

3. Mix a little red lead with water, add some nitric acid, heat gently for a quarter of an hour, filter off the brown powder, wash it with hot water, and dry it. This is PbO_2. The solution contains lead nitrate. Allow it to crystallise. Examine the crystals and compare them with crystals of barium nitrate.

Lead Sulphate, $PbSO_4$, occurs native as *Lead-vitriol* or *Anglesite* in transparent rhombic crystals isomorphous with cælestin, $SrSO_4$, and heavy spar, $BaSO_4$, and is obtained as a white powder soluble in alkalis, by precipitating a lead salt with sulphuric acid or a soluble sulphate.

Lead Nitrate, $Pb(NO_3)_2$, may be obtained by dissolving lead carbonate in nitric acid, or by acting directly upon the metal with the same agent aided by heat : it is, as already noticed, a bye-product in the preparation of the dioxide. It crystallises in anhydrous octahedrons, which are usually milk-white and opaque. It dissolves in 7½ parts of cold water, and is decomposed by heat, yielding nitrogen tetroxide, oxygen, and lead monoxide, which obstinately retains traces of nitrogen.

Experiments.—Dissolve with the aid of heat a few scraps of thin sheet-lead in nitric acid diluted with three or four times its volume of water. Nitric oxide gas is evolved. Crystallise out the salt, examine the crystals and redissolve them in distilled water. Then placing portions of the solution in separate test-tubes, add hydrochloric acid, dilute sulphuric acid, potassium iodide, and hydrogen sulphide, and observe the effect in each case, referring to the text for an account of the compounds formed.

When a solution of lead nitrate is boiled with an additional quantity of lead oxide, a portion of the latter is dissolved, and a basic nitrate generated, which may be obtained in crystals. Carbonic acid separates this excess of oxide in the form of a white compound of carbonate and hydrate of lead.

By boiling a solution of lead nitrate for several hours with lead-turnings, a number of basic nitrates and nitrites of lead may be obtained. As the action progresses, the amount of nitrate and oxide

or hydroxide in the salts produced increases continually in proportion to the nitrate.

Lead Phosphates.—The *Normal Orthophosphate*, $Pb_3(PO_4)_2$, is obtained as a white precipitate on adding ordinary sodium phosphate to a solution of lead acetate. A boiling solution of lead nitrate mixed with phosphoric acid yields a glittering white crystalline precipitate of an acid phosphate, $HPbPO_4$. A phosphato-chloride of lead, $Pb_3(PO_4)_2,Pb_2(PO_4)Cl$, occurs native as *pyromorphite*, and the corresponding arsenato-chloride as *mimetesite*. In both these minerals a portion of the chloride is usually replaced by fluorine.

Lead Silicates.—Silica fuses with lead oxide to a yellow glass. Lead silicate forms a constituent of flint-glass.

Lead Carbonates.—The *Normal Salt*, $PbCO_3$, occurs native as *cerusite* in white rhombic crystals isomorphous with arragonite; also in pseudomorphs after galena and lead sulphate. The same compound is formed by precipitating a cold solution of lead acetate with carbonate of ammonia, and by passing carbon dioxide into a dilute solution of normal lead acetate.

Lead forms several basic carbonates, the most important of which, known as *White Lead*, is manufactured on a very large scale for the use of the painter. Of the many methods put in practice, or proposed, for making white lead, the two following are the most important. One of these consists in forming a basic nitrate or acetate of lead by boiling finely powdered litharge with the normal salt. This solution is then brought into contact with carbon dioxide gas, whereby all the excess of oxide previously taken up by the normal salt is at once precipitated as white lead, and the solution strained or pressed from the latter is again boiled with litharge and treated with the gas, these processes being susceptible of indefinite repetition.

The second, usually known as the Dutch method, and by far the more ancient is rather more complex, and at first sight not very intelligible. A great number of earthen jars are prepared, into each of which is poured a few ounces of crude wood-vinegar; a roll of sheet-lead is then introduced in such a manner that it shall neither touch the vinegar nor project above the top of the jar. The vessels are next arranged in a large building, side by side, upon a layer of stable manure, or better, spent tan, and closely covered with boards. A second layer of tan is spread upon the top of the latter, and then a second series of pots; these are in turn covered with boards and decomposing bark, and in this manner a pile of many alternations is constructed. After the lapse of a few months, the pile is taken down, and the sheets of lead are removed and carefully unrolled; they are then found to be in great part converted into carbonate, which merely requires washing and grinding to be fit for use. The nature of this curious process is generally explained by supposing that the vapour of vinegar raised by the high temperature due to

the fermentation of the tan, together with the oxygen of the air present, gives rise to the formation of basic acetate of lead, which by contact with the carbon dioxide likewise evolved from the decomposing organic matter, is converted into basic carbonate.

White lead is a white heavy amorphous powder, appearing under the microscope as an aggregate of round transparent globules, having a diameter of one to four hundred-thousandths of an inch. The product obtained by the method above-described is generally preferred to those obtained by other processes, on account of its superior opacity or "body." Commercial white lead, however prepared, always contains a certain proportion of hydroxide.

When clean metallic lead is put into pure water and exposed to the air, a white crystalline scaly powder begins to show itself in a few hours, and very rapidly increases in quantity. This substance may consist of lead hydroxide, formed by the action of the oxygen dissolved in the water upon the lead. It is slightly soluble, and may be readily detected in the water. In most cases, however, the formation of this deposit is due to the action of the carbonic acid dissolved in the water: it consists of carbonate in combination with hydroxide, and is nearly insoluble in water. When common river or spring water is substituted for the pure liquid, this effect is less observable, the little sulphate almost invariably present causing the deposition of a very thin but closely adherent film of lead sulphate upon the surface of the metal, which protects it from further action. It is on this account that leaden cisterns are used with impunity, at least in most cases, for holding water: if the latter were quite pure, it would be speedily contaminated with lead, and the cistern would be soon destroyed. Natural water highly charged with carbonic acid cannot under any circumstances be kept in lead or passed through leaden pipes with safety, the carbonate, though insoluble in pure water, being slightly soluble in water containing carbonic acid.

Lead Sulphide, PbS, occurs native as *galena* in cubes or other forms of the regular system, having a bluish-grey colour, and a density of 7·25 to 7·7. The same compound is obtained in crystalline form by passing sulphur-vapour over metallic lead, the combination being attended with vivid combustion; also by fusing lead oxide with excess of sulphur; and as a black amorphous precipitate by passing hydrogen sulphide into a solution of nitrate or acetate of lead. A *chlorosulphide*, $PbCl_2,3PbS$, is obtained as a red precipitate on passing a small quantity of hydrogen sulphide into the solution of a lead salt containing hydrochloric acid. An excess of hydrogen sulphide converts it into the sulphide.

The soluble salts of lead behave with reagents as follows:—

Caustic *potash* and *soda* precipitate a white hydroxide freely soluble in excess. *Ammonia* gives a similar white precipitate not soluble in excess. The *carbonates of potassium*, *sodium*, and *ammonium* precipitate lead carbonate, insoluble in excess. *Sulphuric acid* or a *sulphate* causes a white precipitate of lead sulphate, insoluble

in nitric acid. *Hydrogen sulphide* and *ammonium sulphide* throw down black lead sulphate. Lead is readily detected before the blow-pipe by fusing the compound under examination on charcoal with sodium carbonate, when a bead of metal is easily obtained, which may be recognised by its chemical as well as by its physical properties.

THALLIUM.

Symbol, Tl. Atomic weight, 204.

This element was discovered by Crookes, in 1861, in the seleniferous deposit of a lead-chamber of a sulphuric acid factory in the Hartz mountains, where iron pyrites is used for the manufacture of sulphuric acid. The name is derived from θαλλός, a green shoot or branch, because the existence of this metal was first recognised by an intense green line, appearing in the spectrum of a flame in which thallium is volatilised. It was first suspected to be a non-metallic element, but further examination proved it to be a true metal. It was first obtained in a distinct metallic form by Crookes towards the end of the year 1861, and soon afterwards by Lamy, who prepared it from the deposit in the lead-chamber of M. Kuhlmann of Lille, where Belgian pyrites is employed for the manufacture of sulphuric acid.

Thallium appears to be very widely diffused as a constituent of iron and copper pyrites, though it never constitutes more than the 4000th part of the bulk of the ores. It has also been found in lepidolite from Moravia, in mica from Zinnwald in Bohemia, and in the mother-liquors of the salt-works at Nauheim.

Thallium is most economically prepared from the flue-dust of pyrites burners. This substance is stirred up in wooden tubs with boiling water, and the clear liquor, siphoned off from the deposit, is mixed with excess of strong hydrochloric acid, which precipitates impure thallium monochloride. To obtain a pure salt, this crude chloride is added by small portions at a time to half its weight of hot oil of vitriol in a porcelain or platinum dish, the mixture being constantly stirred, and the heat continued till the whole of the hydrochloric acid and the greater portion of the excess of sulphuric acid are driven off. The fused acid sulphate is now to be dissolved in an excess of water, and an abundant stream of hydrogen sulphide passed through the solution. The precipitate, which may contain arsenic, antimony, bismuth, lead, mercury, and silver, is separated by filtration, and the filtrate is boiled till all free hydrogen sulphide is removed. The liquid is now to be rendered alkaline with ammonia, and boiled; the precipitate of iron oxide and alumina, which generally appears in this place, is filtered off; and the clear solution evaporated to a small bulk. Thallium sulphate then separates on cooling, in long clear prismatic crystals.

Metallic thallium may be reduced from the solution of the sulphate either by electrolysis or by the action of zinc.

Thallium is a heavy metal, resembling lead in its physical properties. When freshly cut, it exhibits a brilliant metallic lustre and greyish colour, somewhat between that of silver and that of lead, assuming a slight yellowish tint by friction with harder bodies. It is very soft, being readily cut with a knife, and making a streak on paper like plumbago. It is very malleable, is not easily drawn into wire, but may be readily squeezed into that form by the process technically called "squirting." It has a highly crystalline structure, and crackles like tin when bent. It melts at 294°.

In contact with the air, thallium tarnishes more rapidly than lead, becoming coated with a thin layer of oxide, which preserves the rest of the metal.

The most characteristic property of thallium is the bright green colour which the metal or any of its compounds imparts to a colourless flame; and this colour, when viewed by the spectroscope, is seen to be absolutely monochromatic, appearing as one intensely brilliant and sharp green line.

Thallium dissolves in hydrochloric, sulphuric, and nitric acids, the latter attacking it very energetically, with copious evolution of red vapours.

Thallium forms two classes of compounds—namely, the thallious compounds, in which it is univalent: and the thallic compounds, in which it is trivalent. Thus it forms two oxides, Tl_2O and Tl_2O_3, with corresponding chlorides, bromides, iodides, and oxygen-salts. In some of its chemical relations it resembles the alkali-metals, forming a readily soluble and highly alkaline monoxide, a soluble and alkaline carbonate, an insoluble platinochloride, a thallio-aluminic sulphate, similar in form and composition to common potash alum, and several phosphates exactly analogous in composition to the phosphates of sodium. In most respects, however, it is more nearly allied to the heavy metals, especially to lead, which it resembles closely in appearance, density, melting-point, specific heat, and electric conductivity; also in giving a black precipitate with hydrogen sulphide, and a white precipitate with soluble chlorides.

Thallium Chlorides.—Thallium forms four chlorides, represented by the formulæ $TlCl$, Tl_4Cl_6, Tl_2Cl_4, and $TlCl_3$; the second and third of which may be regarded as compounds of the monochloride and trichloride.

The *Monochloride* or *Thallious Chloride*, $TlCl$, is formed by direct combination, the metal burning when heated in chlorine gas; or as a white curdy precipitate resembling silver chloride, by treating the solution of any thallious salt with a soluble chloride. When boiled with water it dissolves like lead chloride, and separates in white crystals on cooling. It forms double salts with trichloride of gold and tetrachloride of platinum. The *platinum salt*, $2TlCl,PtCl_4$

separates as a pale yellow, very slightly soluble, crystalline powder, on adding platinic chloride to thallious chloride.

The *Trichloride* or *Thallic Chloride*, $TlCl_3$, is obtained by dissolving the trioxide in hydrochloric acid, or by acting upon thallium, or one of the lower chlorides, with a large excess of chlorine at a gentle heat. It is soluble in water, and separates by evaporation in a vacuum in hydrated crystals ; it melts easily, and decomposes at a high temperature. It forms crystalline double salts with the chlorides of the alkali-metals.

The *Sesquichloride*, $Tl_4Cl_6 = TlCl_3,3TlCl$, is produced by dissolving thallium or the monochloride in nitromuriatic acid, and separates on cooling in yellow crystalline scales. By aqueous ammonia, potash, or even by thallious oxide, it is instantly decomposed into sesquioxide and monochloride, according to the equation :

$$2Tl_4Cl_6 + 3KHO = Tl_2O_3 + 6TlCl + 3KCl + 3HCl.$$

The *Dichloride*, $Tl_2Cl_4 = TlCl_3,TlCl$, is formed by carefully heating thallium or the monochloride in a slow current of chlorine. It is a pale-yellow substance reduced to sesquichloride by further heating.

The **Bromides** of thallium resemble the chlorides.

Iodides.—*Thallious Iodide*, TlI, is formed by direct combination of its elements, or by double decomposition. It forms a beautiful yellow powder, rather darker than sulphur, and melting, below redness, to a scarlet liquid, which, as the mass cools, remains scarlet for some time after solidification, then changes to bright yellow. The dried precipitate, when spread on paper with a little gum-water, undergoes a similar but opposite change to that experienced by mercuric iodide when heated, the yellow surface when held over a flame suddenly becoming scarlet, and frequently remaining so after cooling for several days ; hard friction with a glass rod, however, changes the scarlet colour back to yellow. It is very slightly soluble in water, requiring, according to Crookes, 4453 parts of water at 17·2°, and 842·4 parts at 100°, to dissolve it.

Thallic Iodide, TlI_3, is formed by the action of thallium on iodine dissolved in ether, as a brown solution which gradually deposits rhombic prisms. It forms crystalline compounds with the iodides of the alkali-metals.

Thallium Oxides.—Thallium forms a monoxide and a trioxide.

The *Monoxide* or *Thallious Oxide*, Tl_2O, constitutes the chief part of the crust which forms on the surface of the metal when exposed to the air. It may be prepared by allowing granulated thallium to oxidise in warm moist air, and then boiling with water. The filtered solution first deposits white needles of thallium carbonate, and, on further cooling, yellow needles of the hydroxide, TlHO, which, when left over oil of vitriol in a vacuum, yields the anhydrous monoxide as a reddish-black mass retaining the shape

of the crystals. It is partially reduced to metal by hydrogen at a red heat. When fused with sulphur it yields thallious sulphide. It dissolves readily in water, forming a colourless strongly alkaline solution, which reacts with metallic salts very much like caustic potash. This solution treated with zinc, or subjected to electrolysis, yields metallic thallium.

The *Trioxide* or *Thallic Oxide,* is the chief product obtained by burning thallium in oxygen gas. It is best prepared by adding potash to the solution of a thallic salt, and drying the precipitate at 260°. It is also formed by electrolysis of thallious sulphate. It is a dark-red powder reduced to thallious oxide at a red heat; neutral, insoluble in water and in alkalis. Thallic hydrate, $Tl'''O(HO)$, is obtained by drying the above-mentioned precipitate at 100°.

Thallium Sulphates.—Thallious sulphate, Tl_2SO_4, obtained by evaporating the chloride or nitrate with sulphuric acid, or by heating metallic thallium with that acid, crystallises in anhydrous rhombic prisms, isomorphous with potassium sulphate. It forms, with aluminium sulphate, the salt, $AlTl(SO_4)_2,12H_2O$, isomorphous with common alum; and with the sulphates of magnesium, nickel, etc., double salts containing 6 molecules of water, and isomorphous with magnesium and potassium sulphate, etc. — *Thallic sulphate*, $Tl_2(SO_4)_3,7H_2O$, separates by evaporation from a solution of thallic oxide in dilute sulphuric acid, in thin colourless laminæ, which are decomposed by water, even in the cold, with separation of brown thallic oxide.

Thallium Phosphates.—The thallious phosphates form a series nearly as complete as those of the alkali-metals, which they also resemble in their behaviour when heated. There are three *ortho-phosphates*, containing respectively H_2TlPO_4, HTl_2PO_4, and Tl_3PO_4, The first two are soluble in water; the second is obtained by neutralising boiling dilute phosphoric acid with thallious carbonate, and the first by mixing the dithallious salt with excess of phosphoric acid. The *trithallious salt*, Tl_3PO_4, is very sparingly soluble, and is formed as a crystalline precipitate on mixing the saturated solutions of ordinary disodic phosphate and thallious sulphate; also, together with ammonio-thallious phosphate, by treating the monothallious or dithallious salt with excess of ammonia. There are two *thallious pyrophosphates*, $H_2Tl_2P_2O_7$, and $Tl_4P_2O_7$, both very soluble in water: the first produced by carefully heating monothallious orthophosphate, the second by strongly heating dithallious orthophosphate. Of *thallious metaphosphate*, $TlPO_3$, there are two modifications: the first remaining as a slightly soluble vitreous mass when monothallious orthophosphate is strongly ignited, the second obtained is an easily soluble glass by igniting ammonio-thallious orthophosphate.

Thallic Orthophosphate, $Tl'''PO_4,2H_2O$, separates as an insoluble gelatinous precipitate on diluting a solution of thallic nitrate mixed with phosphoric acid.

Thallious Carbonate, Tl_2CO_3, is deposited in crystals, apparently trimetric, when a solution of thallious oxide is exposed to the air. It is soluble in water, and the solution has a slightly caustic taste and alkaline reaction.

Thallium Sulphide, Tl_2S.—This compound is precipitated from all thallious salts by ammonium sulphide, and from the acetate, carbonate, or oxalate, by hydrogen sulphide (incompletely also from the nitrate, sulphate, or chloride), in dense flocks of a greyish or brownish-black colour. Thallic salts appear to be reduced to thallious salts by boiling with ammonium sulphide. Thallium sulphate projected into fused potassium cyanide is reduced to sulphide, which then forms a brittle metal-looking mass, having the lustre of plumbago, and fusing more readily than metallic thallium.

Reactions of Thallium Salts.—The reactions of thallious salts with hydrogen sulphide and ammonium sulphide have just been mentioned.—From their aqueous solutions thallium is rapidly precipitated in metallic crystals by *zinc*, slowly by *iron*. *Soluble chlorides* precipitate difficultly soluble white thallious chloride; soluble *bromides* throw down white, nearly insoluble bromide; soluble *iodides* precipitate insoluble yellow thallious iodide. Caustic *alkalis* and *alkaline carbonates* form no precipitate; *sodium phosphate* forms a white precipitate, insoluble in ammonia, easily soluble in acid.

Potassium chromate gives a yellow precipitate of thallious chromate, insoluble in cold nitric or sulphuric acid, but turning orange-red on boiling in the acid solution.—*Platinic chloride* precipitates a very pale-yellow insoluble double salt.

Thallic salts are easily distinguished from thallious salts by their behaviour with alkalis, and with soluble chlorides or bromides. Their solutions give with *ammonia*, and with *fixed alkalis* and their *carbonates*, a brown gelatinous precipitate of thallic oxide, containing the whole of the thallium. Soluble *chlorides* or *bromides* produce no precipitate in solutions of pure thallic salts; but if a thallious salt is likewise present, a precipitate of sesquichloride or sesquibromide is formed. *Oxalic acid* forms in solutions of thallic salts a white pulverulent precipitate; *phosphoric acid* a white gelatinous precipitate; and *arsenic acid* a yellow gelatinous precipitate. Thallic nitrate gives with *potassium ferrocyanide* a green, and with the *ferricyanide* a yellow precipitate.

In examining a mixed metallic solution, thallium will be found in the precipitate thrown down by ammonium sulphide, together with iron, nickel, manganese, etc. From these metals it may be easily separated by precipitation with potassium iodide or platinic chloride, or by reduction to the metallic state with zinc.

Thallium salts are reduced before the blow-pipe with charcoal and sodium carbonate or potassium cyanide. The green colour imparted to flame by thallium, and the peculiar character of its spectrum, have already been mentioned.

METALS OF THE COPPER GROUP.

Copper—Silver.

THESE metals do not decompose steam at a red heat. They are precipitated from their solutions in the metallic state by zinc, iron, and the more oxidable metals, and their lower chlorides, like those of the preceding group, are nearly insoluble in water.

Copper, like mercury, forms two classes of salts, the constitution of which is best represented by regarding the metal in both series as a diad.

Cupric salts are generally more stable than cuprous compounds.

Silver forms only one well-defined series of salts, and these correspond in composition to cuprous and mercurous compounds with which in many cases they agree more or less in properties. It is customary to represent silver as a monad metal, but in the absence of positive evidence in favour of that view, and considering the close agreement of silver compounds with those of copper and mercury, it would be more rational to assume a diad character for silver also. The chloride would then be formulated, not as AgCl, but as Ag_2Cl_2, and the constitution would probably be expressed as follows:

$$\begin{array}{l} Ag.Cl \\ | \\ Ag.Cl \end{array} \quad \text{corresponding to} \quad \begin{array}{l} Cu.Cl \\ | \\ Cu.Cl \end{array} \quad \text{and} \quad \begin{array}{l} Hg.Cl \\ | \\ Hg.Cl. \end{array}$$

COPPER.

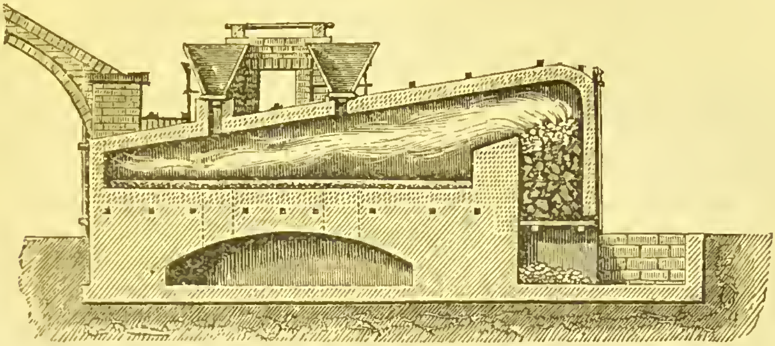
Symbol, Cu (Cuprum). Atomic weight, 63·3.

Copper was known to the ancient Greeks and Romans, and in the form of bronze was used for making weapons in prehistoric times, before the discovery of methods of working iron. The name *Cuprum* is said to have been derived from Æs Cyprium or brass of Cyprus, where in Roman times much copper ore was found.

Copper is a metal of great value in the arts; it sometimes occurs in the metallic state, crystallised in octahedrons, or more frequently in dodecahedrons, but is more abundant in the form of red oxide, and in that of sulphide combined with sulphide of iron, as *yellow copper ore* or *copper pyrites*. Metallic copper occurs in large quantity on the shores of Lake Superior, and in smaller amount mixed with ores of the metal in other parts of the world. Large quantities of copper ores were formerly obtained from the Cornish mines, and taken to South Wales for reduction. The amount of copper obtained from British ores is, however, now comparatively small. Large quantities of valuable ore, chiefly carbonate and red oxide, are obtained from Spain, from South Australia, and Chili. The crude metal is also largely imported and refined in this country.

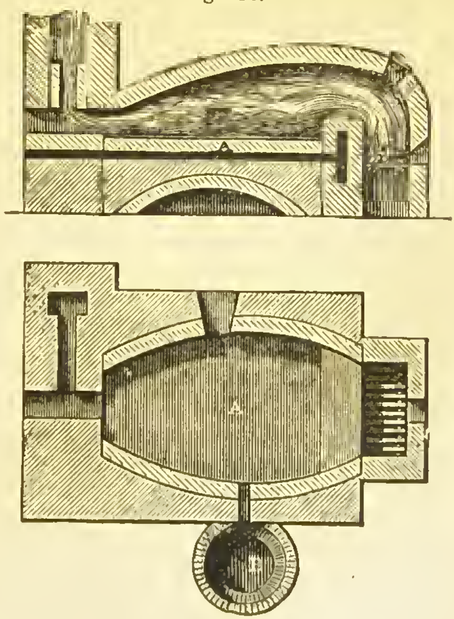
The principle of the process of reduction may be easily made intelligible. It depends upon the fact that, if a mixture of oxides and sulphides of iron and copper are submitted to the action of heat,

Fig. 135.



the iron tends to become converted first into oxide, while the copper retains the sulphur. The processes, which in detail appear somewhat complex, consist of a series of alternate roastings and fusions, performed in separate reverberatory furnaces. The accompanying figure represents a section of the roasting-furnace, the hearth of which is wide and spacious. Here a little sulphur is burnt off, arsenic is expelled, and a portion of the iron oxidised. The next step is fusion of the roasted ore, together with siliceous slag, in a furnace represented both in section and in plan in fig. 136. The products are mainly a fusible mixture of sulphides of copper and iron, forming what is known as ' coarse metal," and a slag consisting of silicate of iron, which is thrown away. The *coarse metal* is run off into water, by which it is granulated, and then subjected to a second roasting and fusion, whereby nearly the whole of the iron is oxidised, and a comparatively pure sulphide of copper called *fine* or *white metal* is obtained. The sulphide of copper is then roasted again and subsequently melted, and in this

Fig. 136.



part of the operation metallic copper, for the first time, separates out as a result of chemical changes similar to those which occur in the reduction of lead. A portion of the sulphide of copper having been converted into oxide, this in its turn reacts upon the sulphide, and produces metallic copper and sulphurous oxide :—

$$2Cu_2O + Cu_2S = SO_2 + 6Cu.$$

The metal is lastly refined by melting in a stream of air, whereby the impurities are oxidised and removed. The last part of the operation consists in thrusting into the melted metal a pole of birchwood, the object of which is to reduce a little remaining oxide by the combustible gases thus generated.

Another process, known as the Mansfeld process, and especially adapted for working the cupriferous schists of Mansfeld in Prussia, which are mostly poor in copper, has long been practised in that locality and in other parts of Europe. The ore, called "Kupferschiefer," is first roasted in heaps, whereby the bituminous matter contained in it is burned away, while water and arsenic are expelled, together with part of the sulphur. The roasted ore is then mixed with 5 to 8 parts of slag and fluor-spar and heated in a blast- or cupola-furnace from 16 to 30 feet high, the coarse metal or "Rohstein" thereby reduced running into basins placed to receive it. This coarse metal, containing from 20 to 60 per cent. of copper, according to the nature of the ore, is next roasted, and the product is melted for fine metal or "Spurstein."

Extraction in the Wet Way.—This mode of treatment is applied to copper ores which are too poor in copper to yield a profitable return by either of the methods above described, especially to the oxide of iron, technically called burnt pyrites or *blue billy*, enormous quantities of which are obtained as residue in the burning of iron pyrites for the manufacture of sulphuric acid (p. 130). When this oxide, which contains a small proportion of copper, is mixed with coarsely crushed rock-salt, and calcined, the copper is converted into soluble cupric chloride, $CuCl_2$, and on lixiviating the calcined mass with water, a solution is obtained, from which the copper may be thrown down in the metallic state by scrap iron. According to another process, invented by Hunt and Douglas, the ores, if they consist wholly of oxides and carbonates, are simply heated, whereas if they contain sulphides they are roasted. In either case, the product is treated with a solution of common salt or calcium chloride and ferrous sulphate, whereby the copper oxides are converted into chlorides. If cuprous oxide is present, metallic copper is at once precipitated, according to the equation $3Cu_2O + 2FeCl_2 = 2Cu_2Cl_2 + Fe_2O_3 + Cu_2$. Cupric oxide, on the other hand, yields cupric and cuprous chlorides, thus: $3CuO + 2FeCl_2 = CuCl_2 + Cu_2Cl_2 + Fe_2O_3$. The cuprous chloride, though insoluble in pure water, is held in solution in presence of the other chlorides, and is decomposed by iron at the same time as the cupric chloride. In addition to the process of refining already mentioned, copper is now to a consider-

able extent refined by a process of electrolysis. Bars of crude Chili or Japan copper are suspended in a solution of copper sulphate, and close to them thin sheets of refined copper. On making the crude copper the anode, while the pure sheet is the cathode of the arrangement, the copper of the impure mass is transferred to the surface of the sheet, while the impurities pass into solution or fall to the bottom of the vat as a dark powder of very complex composition.

Properties of Copper.—Copper has a well-known yellowish-red colour, a density 8·95, and is very malleable and ductile: it is an excellent conductor of heat and electricity; it melts at a bright red heat (about 1090°), and seems to be slightly volatile at a very high temperature.

Copper undergoes no change in dry air: exposed to a moist atmosphere, it becomes covered with a strong adherent green crust, consisting in a great measure of carbonate. Heated to redness in the air, it is quickly oxidised, becoming covered with a black scale. Dilute sulphuric and hydrochloric acids scarcely act upon copper; boiling oil of vitriol attacks it, with evolution of sulphurous oxide; nitric acid, even dilute, dissolves it readily with evolution of nitric oxide.

The alloys of copper are of great importance. *Brass* consists of copper alloyed with from 28 to 34 per cent. of zinc; the latter may be added directly to the melted copper, or granulated copper may be heated with calamine and charcoal-powder, as in the old process. *Gun-metal*, a most valuable alloy, consists of 90 parts copper and 10 tin. *Bell* and *speculum metal* contain a still larger proportion of tin; these are brittle, especially the last named. A good bronze for statues is made of 91 parts copper, 2 parts tin, 6 parts zinc, and 1 part lead; The *brass* or *bronze* of the ancients is an alloy of copper with tin, often also containing lead, and sometimes zinc.

Copper, in its most stable compounds, the cupric compounds, is bivalent, these compounds containing 1 atom of the metal combined with 2 atoms of a univalent, or 1 atom of a bivalent negative radicle, *e.g.*, $CuCl_2$, CuO, $Cu(NO_3)_2$, $CuSO_4$, etc. It also forms another series, the cuprous compounds, in which it may be regarded as univalent, *e.g.*, $CuCl$, Cu_2O, etc., like silver in the argentic compounds. On the other hand, the cuprous componnds may be supposed to be formed by addition of copper to the cupric compounds, the metal still remaining bivalent; thus cuprous chloride, $Cu_2Cl_2 = \begin{array}{c} CuCl \\ | \\ CuCl \end{array}$; cuprous oxide, $Cu_2O = \left.\begin{array}{c} Cu \\ | \\ Cu \end{array}\right> O$. These compounds are fairly stable, but are easily converted into cupric compounds by the action of oxidising agents.

Cuprous Hydride, Cu_2H_2.—When a solution of cupric sulphate is heated to about 70°, with hypophosphorous acid, this compound is

deposited as a yellow precipitate, which soon turns red-brown. It gives off hydrogen when heated, takes fire in chlorine gas, and is converted by hydrochloric acid into cuprous chloride, with evolution of a double quantity of hydrogen, the acid giving up its hydrogen as well as the copper hydrate:

$$Cu_2H_2 + 2HCl = Cu_2Cl_2 + 2H_2.$$

This reaction is usually regarded as affording an instance of the union of two atoms of the same element to form a molecule.

Copper Oxides.—Two oxides of copper are known, corresponding with the chlorides; also a *tetrantoxide* or *quadrantoxide*, Cu_4O; and a very unstable dioxide or peroxide, CuO_2, which is said to be formed, as a yellowish-brown powder, by the action of hydrogen dioxide on cupric hydroxide.

Copper Monoxide, *Cupric Oxide*, or *Black Oxide of Copper*, CuO, is prepared by calcining metallic copper at a red heat, with full exposure to air, or, by heating the nitrate to redness, which then suffers complete decomposition. Cupric salts, mixed with caustic alkali in excess, yield a bulky pale-blue precipitate of hydrated cupric oxide, or cupric hydroxide, CuH_2O_2 or CuO,H_2O, which, when the whole is raised to the boiling-point, becomes converted into a heavy black powder: this also is anhydrous oxide of copper, the hydroxide suffering decomposition, even in contact with water. The oxide prepared at a high temperature is perfectly black and very dense. Cupric oxide is soluble in acids, and forms a series of very important salts, isomorphous with the salts of magnesium.

Cuprous Oxide, Cu_2O, also called *Red Oxide*, and *Suboxide of Copper*.—This oxide may be obtained by heating in a covered crucible a mixture of 5 parts of black oxide and 4 parts of fine copper filings; or by adding glucose to a solution of cupric sulphate, and then putting in an excess of caustic potash; the blue solution, heated to boiling, is reduced by the sugar, and deposits cuprous oxide. This oxide often occurs native in beautiful transparent ruby-red crystals, associated with other ores of copper, and can be obtained in the same state by artificial means. It communicates to glass a magnificent red tint, while that given by cupric oxide is green.

Cuprous oxide dissolves in excess of hydrochloric acid, forming a solution of cuprous chloride, from which that compound is precipitated on dilution with water. Most oxygen-acids, namely, sulphuric, phosphoric, acetic, oxalic, tartaric, and citric acids, decompose cuprous oxide, forming cupric salts, and separating metallic copper; nitric acid converts it into cupric nitrate. Hence there are but few cuprous oxygen salts, none indeed excepting the sulphites, and certain double sulphites formed by mixing a cupric solution with the sulphite of an alkali metal, *e.g.*, ammonium-cuprous sulphite, $Cu(NH_4)SO_3$ or $Cu_2(NH_4)_2(SO_3)_2$.

Experiments.—1. Place some scraps of copper foil or wire in a

muffle heated to redness, and leave with free exposure to air for an hour. The metal is converted into black crystalline oxide. Reserve this for use.

2. Half fill a beaker with solution of copper sulphate, add solution of potash till the liquid is strongly alkaline. A blue precipitate, $Cu(HO)_2$, is found. Boil the whole for a few minutes; the blue hydroxide is converted into black oxide.

3. Dissolve in 100 c.c. of water 5 or 6 grams of copper sulphate and an equal quantity of glucose or milk-sugar. Add solution of potash till the liquid is strongly alkaline, clear and dark-blue. Then apply heat. In a few minutes the clear blue solution deposits a precipitate at first yellow, probably $Cu_2(HO)_2$, then red, Cu_2O.

Copper Tetrantoxide, Cu_4O, is formed, according to H. Rose, by the action of a dilute solution of stannous chloride and caustic potash on a solution of copper sulphate, the whole being well cooled. Cupric hydroxide is then first formed and afterwards reduced by the stannous chloride, with formation of potassium stannate:

$$4Cu(OH)_2 + 12KOH + 3SnCl_2 = Cu_4O + 6KCl + 3K_2SnO_3 + 10H_2O.$$

This oxide is an olive-green powder which may be kept unchanged under water, if air be excluded, but oxidises quickly on exposure to air. It is decomposed by dilute hydrochloric acid, according to the equation $Cu_4O + 2HCl = Cu_2Cl_2 + 2Cu + H_2O$, and in like manner by sulphuric acid.

Copper Chlorides.—*Cupric Chloride*, $CuCl_2$, is most easily prepared by dissolving cupric oxide in hydrochloric acid, and concentrating the green solution thence resulting. It forms pale blue crystals, $CuCl_22H_2O$, very soluble in water and in alcohol: it colours the flame of the latter green. When gently heated, it parts with its water of crystallisation and becomes yellowish-brown; at a high temperature it loses half its chlorine, and becomes converted into *cuprous chloride.* The latter is a white fusible substance, but little soluble in water, and prone to oxidation: it is formed when copper filings or copper-leaf are put into chlorine gas: also by precipitating a solution of cupric chloride or other cupric salt, with stannous chloride:

$$2CuCl_2 + SnCl_2 = Cu_2Cl_2 + SnCl_4.$$

A plate of copper immersed in hydrochloric acid in a vessel containing air, becomes covered with white tetrahedrons of cuprous chloride. This compound dissolves in hydrochloric acid, forming a colourless solution, which gradually turns blue on exposure to the air.

A *hydrated cupric oxychloride*, $CuCl_2,3CuH_2O_2$, occurs native as *atacamite.*

Both the chlorides of copper form double-salts with the chlorides of the alkali-metals.

Experiments.—1. *Cupric Chloride.*—Boil in a covered beaker, about 10 grams of black oxide of copper in 20 c.c. of strong hydrochloric acid, mixed with twice its bulk of water till the oxide is dissolved, and leave the solution to crystallise. Drain the crystals thoroughly. Dry a portion in a dish placed in the oven. Then redissolve in water, and notice the curious changes of colour.

2. *Cuprous Chloride.*—Boil the remainder of the crystals with scraps of copper foil and some hydrochloric acid in a flask till the liquid becomes dark-olive coloured, then pour the solution into cold water. A white precipitate of Cu_2Cl_2 is formed, the solution being almost colourless. Place a portion of the liquid with the precipitate in a test-tube, add a few drops of nitric acid and boil; the white precipitate redissolves, giving a blue solution of cupric chloride.

Cupric Oxysalts.—The *Sulphate*, $CuSO_4,5H_2O$, commonly called *blue vitriol*, is prepared by dissolving cupric oxide in sulphuric acid, or by roasting copper pyrites. It is now manufactured by passing sulphur dioxide, air, and steam through a tower filled with granulated metallic copper. Some considerable amount is also obtained in the operation of 'parting' gold from silver and copper by means of hot sulphuric acid (*see* Gold). It forms large blue triclinic prisms, soluble in four parts of cold and two parts of boiling water; when heated to 100° it readily loses four molecules of crystallisation-water, but the fifth is retained with great pertinacity, and is expelled only at a low red heat. At a very high temperature, cupric sulphate is entirely converted into cupric oxide, with evolution of sulphurous oxide and oxygen. Cupric sulphate combines with the sulphates of potassium and of ammonium, forming pale-blue salts, $CuK_2(SO_4)_2,6H_2O$ and $Cu(NH_4)_2(SO_4)_2,6H_2O$, isomorphous with the corresponding magnesium salts.

Cupric Nitrate, $Cu(NO_3),3H_2O$, is easily made by dissolving the metal in nitric acid: it forms deep blue crystals, very soluble and deliquescent. It is highly corrosive. There is also an insoluble basic nitrate having a green colour.

Cupric Arsenite or *Scheele's Green*, $CuHAsO_3$, is a bright-green insoluble powder, prepared by mixing the solution of a cupric salt with an alkaline arsenite.

Cupric Carbonates.—When sodium carbonate is added in excess to a solution of cupric sulphate, the precipitate is at first pale-blue and flocculent, but by warming it becomes sandy, and assumes a green tint; in this state it contains $CuCO_3,CuH_2O_2+H_2O$. This substance is prepared as a pigment. The beautiful mineral *malachite* has a similar composition, but contains no water of crystallisation, its composition being $CuCO_3,CuH_2O_2$. Another natural compound, called *azurite*, not yet artificially imitated, occurs in large transparent crystals of the deepest blue: it contains $2CuCO_3,CuH_2O_2$. *Verditer*, made by decomposing cupric nitrate with chalk, is said, however, to have a somewhat similar composition.

Experiments.—1. Boil 10 grams of copper scraps in 20–25 c.c. of

strong sulphuric acid contained in a small flask till the acid is evaporated almost to dryness. Sulphur dioxide is evolved, the copper being gradually converted into a black mass (containing sulphide), which, if heated long enough with the acid, becomes nearly white ($CuSO_4$). Dissolve the mass in water, by aid of heat if necessary, filter the blue solution and set by to crystallise.

2. Add to the oxide of copper made in a former experiment (p. 432) an equal weight of sulphuric acid and three or four times as much water. Boil till the oxide is dissolved and set aside to crystallise.

3. To the solution of copper sulphate, made by either of the foregoing experiments, add excess of solution of ammonia, sodium carbonate, sodium phosphate, and sodium arsenite, using a fresh portion in a separate test-tube for each experiment.

Copper Sulphides.—There are two well-defined copper sulphides, analogous in composition to cupric and cuprous oxides, and four others, containing larger proportions of sulphur, but of less defined constitution; these latter are precipitated from solutions of cupric salts by potassium pentasulphide.

Cupric Sulphide, CuS, occurs native as *Indigo-copper* or *Covellite*, in soft bluish-black hexagonal plates and spheroidal masses, and is produced artificially by precipitating cupric salts with hydrogen sulphide.

Cuprous Sulphide, Cu_2S, occurs native as *Copper-glance* or *Redruthite*, in lead-grey hexagonal prisms, belonging to the rhombic system; it is produced artificially by the combustion of copper-foil in sulphur vapour, by igniting cupric oxide with sulphur, and by other methods. It is a powerful sulphur-base, uniting with the sulphides of antimony, arsenic, and bismuth, to form several natural minerals. The several varieties of *fahl-ore*, or *tetrahedrite*, consist of cuprous thioantimonite or thioarsenite, in which the copper is more or less replaced by equivalent quantities of iron, zinc, silver, and mercury. The important ore, called *Copper-pyrites*, is a cuproso-ferric sulphide, $Cu'Fe'''S_2$ or Cu_2S,Fe_2S_3, occurring in tetrahedral crystals of the quadratic system, or in irregular masses. Another species of copper and iron sulphide, containing various proportions of the two metals, occurs native, as *Purple-copper* or *Erubescite*, in cubes, octahedrons, and other monometric forms.

Ammoniacal Copper-Compounds.—The chlorides, the sulphate, the nitrate, and other salts of copper, unite with one or more molecules of ammonia, forming, for the most part, crystalline compounds of blue or green colour, some of which may be regarded as salts of metallammoniums (p. 378). Thus cupric chloride forms with ammonia, the compounds, $2NH_3.CuCl_2$, $4NH_3.CuCl_2$, and $6NH_3.CuCl_2$, the first of which may be formulated as *cupro-diammonium chloride*, $(N_2H_6Cu'')Cl_2$. Cupric sulphate forms, in like manner, *cupro-diammonium sulphate*, $(N_2H_6Cu'')SO_4$, which is a deep-blue crystal-

line salt. Cuprous iodide forms with ammonia the compound, $4NH_3,Cu_2I_2$.

Reactions of Copper Salts.—Caustic *potash* gives with cupric salts a pale-blue precipitate of cupric hydroxide, changing to a black anhydrous oxide on boiling.—*Ammonia* also throws down a pale-blue precipitate, probably consisting of a basic salt; but, when in excess, redissolves it, yielding a deep purplish-blue solution.—*Potassium* and *sodium carbonates* give pale-blue precipitates of cupric carbonate, insoluble in excess.—*Ammonium carbonate* the same, but soluble with deep-blue colour.—*Potassium ferrocyanide* gives a fine red-brown precipitate of cupric ferrocyanide.—*Hydrogen sulphide* and *ammonium sulphide* afford black cupric sulphide, insoluble in ammonium sulphide. Metallic *iron* or *zinc* immersed in a solution of a copper salt quickly becomes coated with metallic copper.

Copper and its compounds impart a green colour to flame. Any compound of copper fused with borax in the oxidising blow-pipe flame forms a transparent glass, which is green while hot, but assumes a fine blue colour on cooling. In the reducing flame the glass becomes opaque, and covered on the surface with reddish streaks of cuprous oxide or metallic copper. This last reaction is facilitated by fusing in the bead a small piece of metallic tin. Copper-compounds, mixed with sodium carbonate or potassium cyanide and heated on charcoal before the blow-pipe, yield metallic copper.

SILVER.

Symbol, Ag (Argentum). Atomic weight, 108.

Silver has been known from the earliest times. The alchemists called it *luna*, the moon, and it was ranked with gold as a "noble" metal.

Silver is found in the metallic state, as sulphide, in union with sulphide of antimony and sulphide of arsenic, also as chloride, iodide, and bromide. Among the principal silver mines may be mentioned those of the Hartz mountains in Germany, of Kongsberg in Norway, and, more particularly, of the Andes, in both North and South America.

The greater part of the silver of commerce is extracted from ores so poor as to render any process of *smelting* or fusion inapplicable, even where fuel could be obtained, and this is often difficult to be procured. Recourse, therefore, is had to another method—that of *amalgamation*—founded on the easy solubility of silver and many other metals in metallic mercury.

In Mexico the ore containing small quantities of sulphide and chloride of silver is stamped or ground, together with water, in mills worked by horses or mules; and the fine mud thus produced is

mixed on a floor with 3 to 5 per cent. of common salt, which is thoroughly incorporated with the mass by the treading of mules. The mass is then left to itself for a day, after which mercury is added, together with an impure mixture of cupric and ferric salts called "magistral"; then more mercury; and the heap is again trodden by mules till thoroughly incorporated. The amalgamation being completed, the slimy mass is washed in buddles worked by mules, whereby the lighter particles are washed away, and the heavier amalgam is deposited. The amalgam is next filtered through canvas bags and finally distilled, and the silver which is left behind is melted into bars.

The reactions which take place in this amalgamation process are probably as follows. The sulphates of copper and iron (in the magistral) are converted by the chloride of sodium into the corresponding chlorides, which then react with the silver sulphide, forming silver chloride:

$$2CuCl_2 + Ag_2S = Cu_2Cl_2 + 2AgCl + S,$$

the cuprous chloride thus produced acting further on the silver sulphide and forming more silver chloride:

$$Cu_2Cl_2 + Ag_2S = Cu_2S + 2AgCl.$$

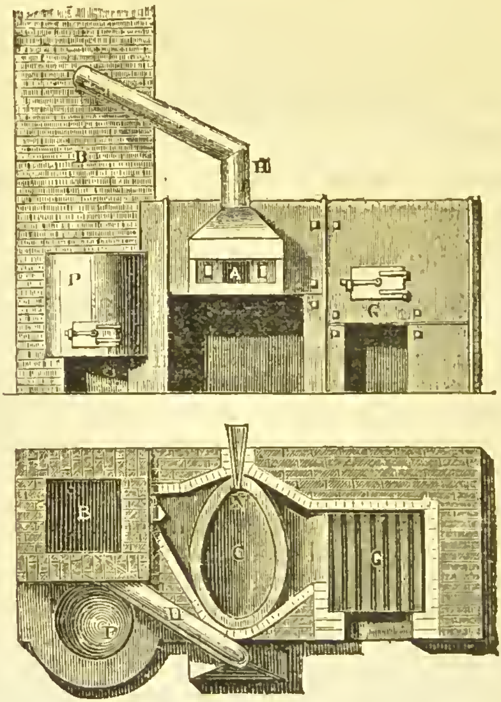
The resulting silver chloride is held in solution by the sodium chloride, and on addition of metallic mercury, is decomposed, yielding calomel and metallic silver. All the mercury thus converted into calomel, amounting to about twice the weight of the silver obtained, is lost.

In Nevada, where the ores are of various degrees of richness, the richer ones are usually roasted wlth common salt, whereby the silver sulphide is converted into chloride; the roasted and pulverised mass is then introduced, together with water, scrap-iron, and mercury, into barrels rotating on a horizontal axis; and the metallic silver thereby set free is dissolved out by mercury. This barrel-process was first worked at Schemnitz in Hungary, and afterwards at Freiberg and Mansfeld, but is now no longer practised in Europe.

A considerable quantity of silver is obtained from argentiferous galena; in fact, almost every specimen of native lead sulphide is found to contain traces of this metal. When the proportion rises to a certain amount, it becomes worth extracting. This is usually accomplished by first concentrating the silver into a portion of the lead by a process of fractional crystallisation, introduced by Mr John Pattinson. The rich lead is then subjected to cupellation. The ore is reduced in the usual manner, the whole of the silver remaining with the lead; the latter is then remelted in a large iron pot, and allowed to cool slowly until solidification commences. The portion which first crystallises is nearly pure lead, the alloy with silver being *more fusible than lead itself:* this is drained away by means of a perforated ladle, and is found to contain nearly the whole of the

silver. The process of cupellation consists in exposing this rich mass to a red heat on the shallow hearth, C, of a furnace (fig. 137), while a stream of air is allowed to impinge upon its surface from the blow-pipe N; oxidation then takes place with great rapidity, the fused oxide or litharge being constantly swept from the metal by the blast, and running off through a channel in the side of the furnace into a pot placed outside. Ultimately the silver, almost chemically pure, and exhibiting a brilliant surface, remains behind. In the

Fig. 137.



figure, G represents the fire-grate, and P a small iron pot with a separate fire, in which the argentiferous lead is usually melted before being introduced into the cupel.

Extraction of Silver in the Wet Way.—Silver may be extracted from argentiferous copper pyrites: (1) By roasting the ore, whereby the sulphides of copper and iron are converted into insoluble oxides, while the silver is obtained as soluble sulphate, from the solution of which, obtained by lixiviating the roasted ore with hot water, the silver is easily precipitated in the metallic state. (2) By roasting the ore with sodium chloride, to convert the silver into chloride, dissolving out this compound with sodium thiosulphate; precipitating the silver from the resulting solution as sulphide by means of

sodium sulphide; and strongly heating the precipitated sulphide in a muffle furnace, whereby the sulphur is burnt away, and the silver is left. (3) By Claudet's process, which is applied to the extraction of the small quantity of silver contained in the burnt pyrites of the sulphuric acid works. The cupreous tank-liquors obtained in this process contain the silver as chloride, held in solution by sodium chloride; and from this solution the silver may be thrown down, in the form of iodide, by adding a solution of an iodide, usually iodide of zinc; a very small quantity of gold is precipitated at the same time.

Purification.—Pure silver is easily obtained. The impure metal is dissolved in nitric acid: if it contains copper, the solution will have a blue tint; gold will remain undissolved as a black powder. The solution is mixed with hydrochloric acid or with common salt, and the white, insoluble, curdy precipitate of silver chloride is washed and dried. This is then mixed with about twice its weight of anhydrous sodium carbonate, and the mixture, placed in an earthen crucible, is gradually raised to a temperature approaching whiteness, during which the sodium carbonate and the silver chloride react upon each other; carbon dioxide and oxygen escape, while metallic silver and sodium chloride result: the former melts into a button at the bottom of the crucible, and is easily detached. The following is perhaps the most simple method for the reduction of silver chloride. The silver-salt is covered with water, to which a few drops of sulphuric acid are added; a plate of zinc is then introduced; the silver chloride soon begins to decompose, and after a short time is entirely converted into metallic silver. The silver thus obtained is grey and spongy; it is ultimately purified by washing with slightly acidulated water.

Properties.—Pure silver has a perfect white colour and a strong lustre: it is exceedingly malleable and ductile, and is probably the best conductor both of heat and electricity known. Its density is 10·5. In hardness it lies between gold and copper. It melts at a bright red heat. Silver is unalterable by air and moisture: it refuses to oxidise at any temperature, but possesses the remarkable faculty already noticed of absorbing many times its volume of oxygen when strongly heated in an atmosphere of that gas, or in common air. The oxygen is again disengaged at the moment of solidification, and gives rise to the peculiar arborescent appearance often remarked on the surface of masses or buttons of pure silver. The addition of 2 per cent. of copper is sufficient to prevent the absorption of oxygen. Silver oxidises when heated with fusible siliceous matter, as glass, which it stains yellow or orange, from the formation of a silicate. It is but slightly attacked by hydrochloric acid; boiling oil of vitriol converts it into sulphate, with evolution of sulphurous oxide; nitric acid, even dilute and in the cold, dissolves it readily. The tarnishing of surfaces of silver exposed to the air is due to hydrogen sulphide, the metal having a strong attraction for sulphur.

The economical uses of silver are many; it is admirably adapted

for culinary and other similar purposes, not being attacked in the slightest degree by any of the substances used for food. It is necessary, however, to diminish the softness of the metal by a small addition of copper. The standard silver of England contains 7·5 per cent. of copper.

Experiments.—Place in a muffle heated to bright redness three small bone-ash cupels. Into one drop a small piece of pure silver (about ·5 gram), into the second the same quantity of silver with about 3 grams of lead, and into the third a similar quantity of silver, cut from a small silver coin, together with 3 grams of lead. Continue heating till the melted globules are seen to be equally bright, then let them cool. The first contains a bead of silver practically undiminished; in the second also the silver remains, whilst the lead has been wholly couverted into oxide, which has been soaked up by the cupel, forming a yellow stain; in the third there will be a bead of silver surrounded by a black stain formed by the mixed oxides of lead and copper. If the silver in each case has been accurately weighed, and the resulting buttons also weighed, knowledge is obtained of the amount of silver in the coin. This is the *dry* method of silver "assay," and may be applied to argentiferous ores and metals.

Allotropic Silver.—When silver nitrate is mixed with tartaric acid and sufficient ammonia to neutralise the solution, a white precipitate of silver tartrate is formed, which on application of heat is reduced, the silver being deposited as a grey precipitate while a portion adheres to the surface of the containing vessel and produces a shining white metallic mirror. If for the tartrate is substituted a mixture of ferrous sulphate and sodium citrate, a ruby-red solution results, from which silver is deposited as a dark-coloured precipitate, which on drying exhibits the colour of gold. Several other varieties are obtainable, exhibiting bluish-green or red colours by varying the reducing agent and the strength of the solutions. These coloured powders are converted into common grey silver by friction and by the action of various acids.

Silver Chlorides.—Two of these compounds are known, containing respectively 1 and 2 atoms of silver to 1 atom of chlorine; the second, however, is a very unstable compound.

The *Monochloride* or *Argentic Chloride*, $AgCl$, or rather Ag_2Cl_2, that is, $Cl.Ag.Ag.Cl$, is invariably produced when a soluble silver salt and a soluble chloride are mixed. It falls as a white curdy precipitate, quite insoluble in water and nitric acid; one part of silver chloride is soluble in 200 parts of hydrochloric acid when concentrated, and in about 600 parts when diluted with double its weight of water. When heated it melts, and on cooling becomes a greyish crystalline mass, which cuts like horn: it is found native in this condition, constituting the mineral called *horn silver.* Silver chloride is decomposed by light, both in the dry and in the wet

state, very slowly if pure, and quickly if organic matter is present: it is reduced also when put into water with metallic zinc or iron. It dissolves very easily in ammonia and in a solution of potassium cyanide. In analysis the proportion of chlorine or hydrochloric acid in a compound is always estimated by precipitation with silver solution. The liquid is acidulated with nitric acid, and an excess of silver nitrate added; the chloride is collected on a filter, or better by subsidence, then washed, dried, and fused; 100 parts correspond to 24·7 of chlorine, or 25·43 of hydrochloric acid.

Argentous Chloride, $Ag_4Cl_2 = Cl.Ag.Ag.Ag.Ag.Cl$, is obtained by treating the corresponding oxide with hydrochloric acid, or by precipitating an argentous salt—the citrate, for example—with common salt. It is easily resolved by heat or by ammonia into argentic chloride and metallic silver.

Silver Bromide, $AgBr$, or Ag_2Br_2, occurs native in Chili and Mexico as *bromargyrite*, usually in small yellow or greenish masses; also mixed with the chloride as *embolite*. It is obtained, on adding hydrobromic acid or a bromide of alkali-metal to a solution of silver nitrate, as a white curdy precipitate insoluble in nitric acid, nearly insoluble in dilute ammonia—whereby it is distinguished from the chloride—but easily soluble in concentrated ammonia. When suspended in water it is easily decomposed by chlorine; hydrochloric acid gas also decomposes it at 700°, with evolution of hydrobromic acid. The fused bromide is scarcely acted on by light, but the precipitated bromide when exposed to light quickly assumes a greyish-white colour.

Silver Fluoride, AgF, or Ag_2F_2, is produced by dissolving argentic oxide or carbonate in aqueous hydrofluoric acid, and separates on evaporation in transparent quadratic octahedrons, which contain AgF,H_2O, or $Ag_2F_2,2H_2O$, and give off their water when fused. Their solution gives, with hydrochloric acid, a precipitate of argentic chloride.

Silver Iodide, AgI, or Ag_2I_2, is a pale yellow insoluble precipitate, produced by adding silver nitrate to potassium iodide: it is insoluble, or nearly so, in ammonia, and in this respect forms an exception to silver-salts in general. Deville obtained a crystalline silver iodide by the action of concentrated hydriodic acid upon metallic silver, which it dissolves with disengagement of hydrogen. Hydriodic acid converts silver chloride into iodide.

Silver Oxides.—There are three oxides of silver, only one of which, however, can be regarded as a well-defined compound, namely:—

The *Monoxide* or *Argentic Oxide*, $Ag_2O = \left.\begin{array}{l} Ag \\ | \\ Ag \end{array}\right\rangle O$.—This oxide is strongly basic, yielding salts isomorphous with those of the

alkali-metals. It is obtained as a pale-brown precipitate on adding caustic potash to a solution of silver nitrate :

$$2AgNO_3 + KHO = Ag_2O + KNO_3 + HNO_3.$$

It is very soluble in ammonia, and is dissolved also to a small extent by pure water ; the solution is alkaline. Recently precipitated silver chloride, boiled with a concentrated solution of caustic potash, is converted, according to Gregory, although with difficulty, into argentic oxide, which in this case is black and very dense. Argentic oxide neutralises acids completely, and forms, for the most part, colourless salts. It is decomposed by a red heat, with evolution of oxygen, spongy metallic silver being left ; the sun's rays also effect its decomposition to a small extent.

Argentous Oxide, $Ag_4O = \left.\begin{array}{l} Ag{-}Ag \\ | \\ Ag{-}Ag \end{array}\right\rangle O$(?).—When dry argentic citrate is heated to 100° in a stream of hydrogen gas, it loses oxygen and becomes dark-brown. The product, dissolved in water, gives a dark-coloured solution containing free citric acid and argentous citrate, which, when mixed with potash, yields a precipitate of argentous oxide. This oxide is a black powder, very easily decomposed, and soluble in ammonia. The solution of argentous citrate is rendered colourless by heat being resolved into argentic citrate and metallic silver.

Silver Dioxide, $Ag_2O_2 = \begin{array}{lr} Ag{-} & O \\ | & | \\ Ag{-} & O \end{array}$, is a black crystalline substance which forms upon the anode during the electrolysis of a solution of silver nitrate. It is reduced by heat ; evolves chlorine when acted upon by hydrochloric acid ; explodes when mixed with phosphorus and struck ; and decomposes solution of ammonia, with great energy and rapid disengagement of nitrogen gas.

Oxysalts of Silver.—*Silver Sulphate*, Ag_2SO_4, may be prepared by boiling together oil of vitriol and metallic silver, or by precipitating a concentrated solution of silver nitrate with an alkaline sulphate. It dissolves in 88 parts of boiling water, and separates in great measure in the crystalline form on cooling, being but slightly soluble at a low temperature. It forms with ammonia a crystallisable compound which is freely soluble in water, contains $2NH_3,Ag_2SO_4$, and may therefore be regarded as *argentammonium sulphate*, $(NH_3Ag)_2SO_4$.

Silver Dithionate, $Ag_2S_2O_6$, is a soluble crystallisable salt, permanent in the air. The *thiosulphate*, $Ag_2S_2O_3$, is insoluble, white, and very prone to decomposition : it combines with the alkaline thiosulphates, forming soluble compounds distinguished by an intensely sweet taste. The alkaline thiosulphates dissolve both oxide

and chloride of silver, and give rise to similar salts, an oxide or chloride of the alkali-metal being at the same time formed : hence the use of alkaline thiosulphates in fixing photographic pictures (p. 445).

Silver Nitrate, $AgNO_3$, or rather $Ag_2(NO_3)_2$, is prepared by dissolving silver in nitric acid, and evaporating the solution to dryness, or until it is strong enough to crystallise on cooling. The crystals are colourless, transparent, anhydrous tables, soluble in an equal weight of cold and in half that quantity of boiling water ; they also dissolve in alcohol. They fuse when heated, like crystals of nitre, and at a high temperature suffer decomposition : the *lunar caustic* of the surgeon is silver nitrate which has been melted and poured into a cylindrical mould. Pure silver nitrate is unchanged by light, but the salt blackens when exposed to light if organic matters of any kind are present, and it is sometimes employed to communicate a dark stain to the hair ; it enters into the composition of the "indelible" ink used for marking linen. The black stain is thought to be metallic silver.

Experiment.—Dissolve a shilling or two in nitric acid diluted with a little water. Add to the liquid a solution of common salt, till, after well stirring the liquid and letting it stand to become clear, the addition of a drop of the chloride produces no further precipitate. Pour off the clear liquid, collect the chloride of silver on a filter, and wash well with hot water till, on collecting some of the filtrate in a test tube and adding solution of ammonia, no blue colour is perceptible. Then drain and dry the precipitate. Mix it with three times its weight of dry sodium carbonate, and heat the mixture in a clay crucible to bright redness until the whole is completely fused. When cold, break the crucible, extract the button of pure silver, roll it into a strip, and dissolve in a sufficient quantity of pure nitric acid. Evaporate the solution to dryness, redissolve the nitrate in the least possible quantity of distilled water, and let the salt crystallise, or simply preserve the solution for use.

Silver Carbonate is a white insoluble substance obtained by mixing solutions of silver nitrate and sodium carbonate. It is blackened and decomposed by boiling.

Silver Sulphide, Ag_2S, is a soft, grey, and somewhat malleable substance, found native in the crystallised state, and easily produced by melting together its constituents or by precipitating a solution of silver with hydrogen sulphide. It is a strong sulphur-base, and combines with the sulphides of antimony and arsenic : examples of such compounds are found in the beautiful minerals, *dark* and *light red silver ore.*

Silver Nitrate, Ag_3N or Ag_6N_2, *Berthollet's Fulminating Silver.*—This is a black, explosive compound formed by digesting precipitated argentic oxide in ammonia. While moist it explodes only when rubbed with a hard body, but when it is dry, the touch of a

feather is sufficient. The ammonia retains some of this substance in solution, and deposits it in small crystals by spontaneous evaporation. A similar compound exists containing gold.

Ammoniacal Compounds.—Argentic chloride absorbs ammonia gas, forming the compound $3NH_3,Ag_2Cl_2$, which readily gives off its ammonia when heated, and may be used for the preparation of pure ammonia-gas—or of liquid ammonia if heated in a sealed tube. Argentic iodide likewise absorbs ammonia-gas, forming the compound NH_3,Ag_2I_2, which gives off its ammonia on exposure to the air. Silver nitrate produces compounds of a similar kind.

Reactions of Silver Salts.—Soluble silver salts are perfectly characterised by the white curly precipitate of silver chloride, darkening on exposure to light, and insoluble in hot nitric acid, which is produced by the addition of any soluble *chloride.* Lead and mercury are the only metals which can be confounded with silver in this respect; but lead chloride is soluble to a great extent in boiling water, and is deposited in brilliant acicular crystals when the solution cools; and mercurous chloride is instantly blackened by ammonia, whereas silver chloride is dissolved thereby.

Solutions of silver are reduced to the metallic state by *iron*, *copper*, *mercury*, and other metals. They give with *hydrogen sulphide* a black precipitate of argentic sulphide, insoluble in ammonium sulphide; with *caustic alkalis*, a brown precipitate of argentic oxide; and with *alkaline carbonates*, a white precipitate of argentic carbonate, both precipitates being easily soluble in ammonia. Ordinary *sodium phosphate* forms a yellow precipitate of argentic orthophosphate; *potassium chromate* or *dichromate*, a red-brown precipitate of argentic chromate.

Photography.—The processes of photography have been so closely connected with the action of light upon salts of silver, that a short notice of the early stages of development of this important art may be appropriately introduced in this place. In the year 1802 Thomas Wedgwood proposed a method of copying paintings on glass, by placing behind them white paper or leather moistened with a solution of silver nitrate, which became decomposed and blackened by the transmitted light in proportion to the intensity of the latter; and H. Davy, in repeating these experiments, found that he could thus obtain tolerably accurate representations of objects of a texture partly opaque and partly transparent, such as leaves and the wings of insects, and even copy with a certain degree of success the images of small objects obtained by the solar microscope. These pictures, however, required to be kept in the dark, and could be examined only by candle-light, otherwise they became obliterated by the blackening of the whole surface, from which the silver salt could not be removed. These attempts at light-painting attracted but little notice till the year 1839, when Fox Talbot published his plan of "photogenic drawing." This consisted in exposing in the camera a paper soaked in a weak solution of common salt, and afterwards washed over with

a strong solution of silver nitrate; the image thus obtained was a *negative* one, the lights being dark and the shadows light, and the pictures were fixed by immersion in a solution of common salt.

Many improvements have been made in this process. In 1841 Fox Talbot patented the beautiful process known as the "Talbotype or Calotype process," in which the paper is coated with silver iodide by dipping it first in silver nitrate, then in potassium iodide. Paper thus prepared is not sensitive *per se* to the action of light, but may be rendered so by washing it over with a mixture of silver nitrate and gallic or acetic acid. If it be exposed to the camera for two or three minutes, it does not receive a visible image (unless the light has been very strong), but still the compound has undergone a certain change by the influence of the light: for on subsequently washing it over with the mixture of silver nitrate and acetic or gallic acid, and gently warming it, a negative image comes out on it with great distinctness. This image is *fixed* by washing the paper with sodium thiosulphate (commonly called hyposulphite), which removes the whole of the silver iodide not acted upon by the light, and thus protects the picture from further change by exposure to light. The negative picture thus obtained is rendered transparent by placing it between two sheets of blotting-paper saturated with white wax, and passing a moderately heated smoothing-iron over the whole. It may then be used for printing *positive pictures* by laying it on a sheet of paper prepared with chloride or iodide of silver, and exposing it to the sun.

A most important step in the progress of photography was the substitution of a transparent film of iodised collodion or albumin spread upon glass, for the iodised paper used in Talbot's process, to receive the negative image in the camera. The process was thus rendered much more certain and rapid, and the positive pictures obtained by transferring the negative to paper prepared with chloride or iodide of silver, were found to be much sharper in outline than when the transference occurs through paper, as in the Talbotype process. In this process, as in that of the calotype, the image produced in the camera is a latent one, and requires development with substances such as pyrogallic acid, or ferrous sulphate, which, having a tendency to absorb oxygen, induce, in presence of silver nitrate, the reduction of the chloride or iodide to the metallic state. The modern dry-plate processes are based upon the employment of an emulsion of bromide or of chlorobromide of silver with gelatin, which is spread upon glass or paper and dried. The plates thus prepared can be preserved for an indefinite length of time, and are much more sensitive to the action of light than the wet collodion film. For a description of the best apparatus and latest processes used in these methods the reader must consult one of the numerous handbooks of photography.

Sir John Herschel showed that a great number of other substances can be employed in these photographic processes by taking advantage of the deoxidising effects of certain portions of the solar

rays. Paper washed with a solution of ferric salt becomes capable of receiving impressions of this kind, which may afterwards be made evident by potassium ferricyanide, or gold chloride. Vegetable colours are also acted upon in a very curious and apparently definite manner by the different parts of the spectrum.

The *Daguerreotype*, the announcement of which was first made in the summer of 1839, by M. Daguerre, who had been occupied with this subject from 1826, if not earlier, is another remarkable instance of the decomposing effects of the solar rays. A clean and highly polished plate of silvered copper is exposed for a certain time to the vapour of iodine, and then transferred to the camera. In the most improved state of the process, a very short time suffices for effecting the necessary change in the film of silver iodide. The picture, however, becomes visible only by exposing it to the vapour of mercury, which attaches itself, in the form of exceedingly minute globules, to those parts which have been most acted upon, that is to say, to the lights, the shadows being formed by the dark polish of the metallic plate. Lastly, the plate is washed with sodium thiosulphate, to remove the undecomposed silver iodide and render it permanent.

After Daguerre's time this process underwent considerable improvements; amongst these, we may mention the exposure of the plate to the vapour of bromine, by which the sensitiveness of the film is greatly increased, and the reduction of metallic gold upon the surface of the film during the process of fixing, by which the lights and shades of the picture are rendered more effective; but it was long ago completely superseded by photography.

Etching and lithographic processes, by combined chemical and photographic agency, are extensively employed. The earliest was that of Nièpce: he applied a bituminous coating to a metal plate, upon which an engraving was superimposed. The light, being thus partially interrupted, acted unequally upon the varnish; a liquid hydrocarbon, *petroleum*, used as a solvent, removed the bitumen wherever the light had not acted: the unprotected metal was bitten by an acid; and the plate could then be printed from in the usual way.

Fox Talbot introduced the use of a mixture of potassium dichromate and gelatin, which hardens by exposure to the light; the parts not affected are removed by washing.

The bitumen process of Nièpce has been applied to lithographic stone; and positives obtained from negative Talbotypes have been printed off by a modification of the ordinary lithographic process. During the last few years a great number of new processes for the photo-mechanical reproduction of drawings or photographs from nature have been introduced, but for an account of these special technical works must be consulted. (See, for example, the article "Photography" in *Thorpe's Dictionary of Applied Chemistry.*)

METALS OF THE YTTRIUM GROUP.*

A CONSIDERABLE number of metals occurring in gadolinite, cerite, samarskite, and other rare minerals are included in this group: but the position of many of them among the elements is still exceedingly doubtful. The extraction and separation of the oxides of these metals is complex and difficult, and the number of distinct oxides or earths thus obtainable is not exactly known, the discovery of some of them, announced by certain chemists, having been denied by others; but the existence of the eight following may perhaps be considered as established:—

	Symbol.	At w.		Symbol.	At w.
Scandium, .	Sc	44	Samarium (or Decipium ?), . .	Sm	150
Yttrium, .	Y	90	Terbium, . . .	Tb	148
Lanthanum, .	La	138	Erbium, . .	Er	166
Cerium, .	Ce	140	Ytterbium, . .	Yb	173
Didymium, .	Di	140 to 143			

YTTRIUM, ERBIUM, TERBIUM, YTTERBIUM, SCANDIUM.

These metals exist as silicates in the gadolinite or ytterbite of Ytterby in Sweden, and in a few other rare minerals: also as niobates and tantalates in the samarskite of North Carolina.

To obtain the earths yttria and erbia (including terbia and ytterbia), gadolinite is digested with hydrochloric acid, and the solution separated from the silica is treated with oxalic acid, which throws down the oxalates of erbium and yttrium, together with those of calcium, cerium, lanthanum, and didymium. These oxalates are converted into nitrates; the solution is treated with excess of solid potassium sulphate, to separate the cerium metals: the erbia and yttria, which still remain in solution, are again precipitated by oxalic acid; and the same treatment is repeated, till the solution of the mixed earths, when examined by the spectroscope, no longer exhibits the absorption-bands characteristic of didymium. To separate the erbia and yttria, they are again precipitated by oxalic acid. The oxalates are converted into nitrates, and the nitrates of erbium and yttrium are separated by a series of fractional crystallisations, the erbium salt being the less soluble of the two, and crystallising out first.

This process, for the details of which we must refer to larger

* For a general review of the rare earth-metals, see the Biographical Notice of Marignac by Professor Clève.—*Trans. Chem. Soc.*, 1895.

works, effects the separation of yttria from erbia, terbia, and ytterbia; but no method of completely separating the last three earths one from the other has yet been devised. The proportions of these earths in gadolinite are, moreover, variable, some specimens containing nearly pure erbia, whilst others are nearly free from that earth. Ytterbia has been obtained in very small quantity only.

Scandium, Sc. Atomic weight 44·03 (Nilson); 44·91 (Cleve). This metal, discovered by Nilson in 1879, and further examined by Cleve, exists only in gadolinite and yttrotitanite. The metal has not been isolated.

Scandia, Sc_2O_3, may be separated from ytterbia by the readier decomposibility of its nitrate by heat, and by its property of forming an insoluble double salt with potassium sulphate. It is a light, infusible white powder, resembling magnesia, easily soluble in hot nitric and hydrochloric acids, nearly insoluble in the same acids when cold. It is not volatile, and gives no colour to flame, but the chloride gives a very brilliant spectrum with the electric spark.

Scandium salts are colourless, and have a sour astringent taste, quite different from the sweet taste of the salts of yttrium and erbium. With potash and ammonia they give bulky white precipitates, insoluble in excess; tartaric acid prevents the precipitation in the cold, but a precipitate forms on heating. Sodium carbonate gives a precipitate soluble in excess. Ammonium sulphide throws down the hydroxide. Sodium orthophosphate gives a gelatinous precipitate; oxalic acid a curdy precipitate quickly becoming crystalline.

Scandium nitrate crystallises from a strong solution in small prisms. The *sulphate*, $Sc_2(SO_4)_3,8H_2O$, is permanent at ordinary temperatures, but gives off $4H_2O$ at 100°, the rest on gentle ignition; decomposed at a high temperature. The *double sulphate*,

$$K_2Sc_2(SO_4)_4,xH_2O,$$

crystallises in groups of small prisms, very slightly soluble in water, and quite insoluble in a saturated solution of potassium sulphate.

The spectrum of scandium obtained by passing a powerful induction spark between aluminium poles moistened with a solution of the chloride is very complicated, containing more than a hundred lines.

Scandium agrees very closely, in its atomic weight and in the properties of its oxide and salts, with the element whose existence was predicted by Mendelejeff under the name of *Ekabor—e.g.*, in forming a white sesquioxide, infusible, soluble with difficulty in acids after ignition, insoluble in alkaliis; also in forming colourless salts, and a sulphate which unites with potassium sulphate, forming a double salt analogous in composition to common alum.

Erbia, Eb_2O_3, obtained by ignition of erbium nitrate or oxalate, has a faint rose colour.

Erbium salts have a rose-red colour, deeper in the hydrated than in the anhydrous state: they have an acid reaction and sweet astringent taste. The *sulphate*, $EbSO_48H_2O$, forms light rose-coloured crystals, isomorphous with the sulphates of yttrium and didymium.

Yttria, Y_2O_3, is a soft, nearly white powder. It dissolves slowly but completely in hydrochloric, nitric, and sulphuric acids, forming colourless solutions which do not exhibit any absorption-spectrum. *Yttrium sulphate*, $Y_2(SO_4)_3,8H_2O$, forms small colourless crystals.

Terbia, Tb_2O_3, after ignition at a moderate heat, has a deep orange colour, but becomes quite colourless after very strong ignition, or when heated in a stream of hydrogen. It dissolves slowly but completely in the most dilute acids; in hydrochloric acid, with evolution of chlorine. Its solutions are colourless, and show no absorption-spectrum. The *sulphate*, $Tb_2(SO_4)_3, 8H_2O$, forms colourless crystals isomorphous with the sulphates of yttrium, erbium, and didymium.

Ytterbia, Yb_2O_3, is a colourless infusible earth, of sp. gr. 9·175, insoluble in water, easily soluble in dilute acids, and attacked with difficulty, even by strong acids, in the cold. Its solutions have a sweet astringent taste, are colourless, and give no absorption-spectrum. The *sulphate*, $Yb_2(SO_4)_3,8H_2O$, forms large brilliant prisms permanent in the air, but giving off their water at 100°. It dissolves slowly in boiling water, completely in a saturated solution of potassium sulphate.

Cerium—Lanthanum—Didymium—Samarium.

The first three of these metals occur together as silicates in the Swedish mineral cerite, also in allanite, orthite, and a few others: and as phosphates in monazite, edwardsite, and cryptolite, a mineral occurring disseminated through apatite and through certain cobalt ores.

Cerium was discovered in 1803 by Klaproth, and by Hisinger and Berzelius, who obtained it in the form of oxide from cerite. This mineral is completely decomposed by boiling with strong hydrochloric acid, silica being separated, and the cerium, together with iron and other metals, dissolving as chloride. On treating the acid solution thus obtained with oxalic acid, cerium oxalate is precipitated as a white crystalline powder, which, when ignited, leaves a brown oxide. The product thus obtained was for some time regarded as the oxide of a single metal, cerium; but in 1839 and 1841, Mosander showed that it contained the oxides of two other metals, which he designated as lanthanum* and didymium.†

* From λανθάνω, to lie hid. † From δίδυμοι, twins.

Cerium oxide may be separated from the oxides of lanthanum and didymium by treating the crude brown oxide above mentioned, first with dilute and then with strong nitric acid, which gradually removes the whole of the lanthanum and didymium oxides.

The separation of these two oxides one from the other is much more difficult, and can be effected only by successive crystallisation of their sulphates. If the lanthanum salt is in excess, in which case the solution of the mixed sulphates has only a faint amethyst tinge, the liquid is evaporated to dryness, and the residue heated to a temperature just below redness, to render the sulphates anhydrous. The residue thus obtained is then to be added by small portions to ice-cold water, which dissolves it easily, and the resulting solution heated in a water-bath to about 40°. Lanthanum sulphate then crystallises out, containing only a small portion of didymium, and may be further purified by repeating the whole process. If, on the other hand, the didymium salt is in excess, in which case the liquid has a decided rose colour, separation may be effected by leaving the acid solution in a warm place for a day or two. Didymium sulphate then separates in large rhombohedral crystals.

Metallic cerium, lanthanum, and didymium are obtained by reducing the chlorides with sodium, in the form of grey powders, which decompose water at ordinary temperatures, and dissolve rapidly in dilute acids with evolution of hydrogen.

These three metals were originally regarded as diads ; afterwards from Hillebrand's determination of their specific heats, and from the fact that they all three form salts in which the metal is trivalent, they were supposed to be triads ; but experiments by Brauner have shown that lanthanum only is a triad, forming a single series of salts, LaR_3 (R denoting an acid radicle) ; whereas cerium is a tetrad, inasmuch as, besides the chloride Ce_2Cl_6, the oxide Ce_2O_3, etc., it also forms a tetrafluoride CeF_4, and a dioxide CeO_2. Didymium has since been found to consist of at least two elements, *neo-dymium* and *praseo-dymium*, both of which are pentads forming pentoxides Di_2O_5. These metals thus fall regularly into their places in the periodic system (p. 268).

Lanthanum, as already observed, forms only one set of compounds, viz., $LaCl_3$, La_2O_3, $La_2(SO_4)_3$. There is, however, a higher oxide, the composition of which is not exactly known. Lanthanum salts are colourless ; their solutions yield, with alkalis, a precipitate of *lanthanum hydroxide*, LaH_2O_3, which, when ignited, leaves the white anhydrous sesquioxide. Both the hydroxide and the anhydrous oxide dissolve easily in acids. *Lanthanum sulphate* forms small prismatic crystals, containing $La_2(SO_4)_3,9H_2O$. *Lanthanum and potassium sulphate*, $LaK_3(SO_4)_3$ is formed, on mixing the solution of a lanthanum salt with potassium sulphate, as a white crystalline precipitate, resembling the corresponding cerium salt.

Cerium forms two series of compounds, viz., the c e r o u s com-

pounds in which it is trivalent, as above stated, *e.g.*, Ce_2Cl_6, Ce_2O_3, $Ce_2(SO_4)_3$; and the ceric compounds in which it is quadrivalent, *e.g.* ceric oxide, CeO_2, ceric sulphate, $Ce(SO_4)_2$, etc.

Cerous Oxide, Ce_2O_3, is obtained by igniting the carbonate or oxalate in a current of hydrogen, as a greyish-blue powder, quickly converted into ceric oxide on exposure to the air. Its salts are colourless. The *sulphate*, $Ce(SO_4)_3$, crystallises with various quantities of water, according to the temperature at which it is deposited. *Cerium and potassium sulphate*, $CeK_3(SO_4)_3$, separates as a white powder on immersing solid potassium sulphate in a solution of a cerous salt. It is slightly soluble in pure water, but insoluble in a saturated solution of potassium sulphate. The formation of this salt affords the means of separating cerium from most other metals.

Ceric Oxide, CeO_2, is produced when cerous hydroxide, carbonate, or nitrate is ignited in an open vessel. It is yellowish-white, acquires a deep orange-red colour when heated, but recovers its original tint on cooling. It is not converted into a higher oxide by ignition in oxygen. *Hydrated ceric oxide*, $2CeO_2,3H_2O$, obtained by passing chlorine into aqueous potash in which cerous hydroxide is suspended, is a bright yellow precipitate, which dissolves readily in sulphuric and nitric acids, forming yellow solutions of ceric salts; and in hydrochloric acid, with evolution of chlorine, forming colourless cerous chloride.

The solution of the sulphate yields by spontaneous evaporation, first, brown-red crystals of a *ceroso-ceric salt*, $\left.\begin{matrix}Ce_2(SO_4)_3\\2Ce(SO_4)_2\end{matrix}\right\} + 4H_2O$, and afterwards yellow indistinctly crystalline *ceric sulphate*, $Ce(SO_4)_2 + 4H_2O$.

Cerium Fluorides.—The mineral *fluocerite*, found at Finnbo in Sweden, is generally regarded as CeF_4; but the only published analysis of it, by Berzelius, agrees better with the formula, Ce_2F_6,H_2O. When hydrated ceric oxide is treated with aqueous hydrofluoric acid, a brownish powder is obtained, consisting of a hydrated tetrafluoride, CeF_4,H_2O. This compound, when moderately heated, gives off its water and part of its fluorine as hydrofluoric acid, and at a higher temperature it gives off a gas (? fluorine) which decomposes potassium iodide, with liberation of free iodine, these decompositions apparently taking place according to the following equations:—

$$(a)\quad 2(CeF_4,H_2O) = Ce_2F_6 + 2HF + O + H_2O$$
$$(b)\quad 2(CeF_4) = Ce_2F_6 + F_2.$$

On heating the hydrated tetrafluoride for some time in contact with moist air, pure ceric oxide is left: $CeF_4,H_2O + H_2O = CeO_2 + 4HF$. A *potassioceric fluoride*, $3KF,2CeF_4,H_2O$, is obtained, as a yellowish-white crystalline powder, on treating hydrated ceric oxide with a solution of potassium and hydrogen fluoride.

Didymium.—Solutions of didymium salts exhibit a well-marked

absorption spectrum, containing two black lines inclosing a very bright space. One of these black lines is in the yellow, immediately following Fraunhofer's line D ; the other is situated between E and *b*. These characters can be distinctly recognised in a solution half an inch deep, containing only 0·10 per cent. of didymium salt. Lanthanum salts do not exhibit an absorption spectrum.

Auer, in 1885, showed that by fractional crystallisation of the mixed nitrates of ammonium, didymium, and lanthanum, two other bodies might be obtained—the one giving green salts, the other pink salts. These, which have been called respectively praseodymium and neodymium, exhibit characteristic absorption spectra, which, when combined, approximate to the original spectrum of didymium.

Samarium.—This metal, discovered by Lecoq de Boisbaudran in samarskite, by means of its characteristic spectrum, has been further examined by Cleve who obtained its oxide, samaria, from the thorite of Arendal in Norway, in which it exists together with the oxides of thorium, cerium, lanthanum, and didymium.

It is now supposed to be identical with the metal obtained by Delafontaine in the Samarskite of North Carolina, and called decipium.

The spectrum of samarium is distinguished by several bands, among which four in the blue region are the most characteristic. Its atomic weight is about 150, supposing its oxide to have the composition Sm_2O_3, a view which is in accordance with the close analogy of the samarium salts to those of didymium. Samarium is in fact more nearly related to didymium than to any other element.

Samarium Chloride, $SmCl_3,6H_2O$, forms large tabular deliquescent crystals. The *oxide*, Sm_2O_3, is a white powder with a scarcely perceptible tinge of yellow, and easily soluble in acids, forming salts whose solutions have a deep-yellow colour. The crystallised salts are topaz-coloured, but in the state of powder they are yellowish-white. The *hydroxide* is a gelatinous white or faintly yellowish precipitate, insoluble in alkalis. It is a stronger base than yttria, but not so strong as didymia.

The *acetate*, $Sm(C_2H_3O_2)_3+4H_2O$, forms short, well-defined prisms, moderately soluble in water. The *sulphate*, $Sm_2(SO_4)_3,8H_2O$, forms well-defined shining crystals, less soluble in water than in sulphate of didymium. The *double sulphate*, $2Sm_2(SO_4)_3,9K_2SO_4 + 3H_2O$?, was slowly deposited as a white powder on adding samarium acetate to excess of potassium sulphate : it is but very slightly soluble in excess of potassium sulphate. The *oxalate*, $Sm_2(C_2O_4)_3,10H_2O$, is a white or pale-yellowish crystalline precipitate.

METALS OF THE ALUMINIUM GROUP.

Aluminium—Gallium—Indium.

THESE metals are trivalent, forming compounds of the forms MCl_3, M_2O_3, etc. Their oxides are only weakly basic, and their sulphates unite with those of the alkali-metals, forming double salts, called alums, which crystallise in octahedrons and other forms of the regular system.

ALUMINIUM.

Symbol, Al. Atomic weight, 27.

This metal occurs very abundantly in nature in the state of silicate, as in felspar and its associated minerals; also in the various modifications of clay thence derived. It was first isolated by Wöhler, who obtained it as a grey powder by decomposing aluminium chloride with potassium; and H. Sainte-Claire Deville, by an improved process founded on the same principle, succeeded in obtaining it in the compact form and on the manufacturing scale. The process consisted in decomposing the double chloride of aluminium and sodium, $AlCl_3,NaCl$, by heating it with metallic sodium, fluor-spar or cryolite being added as a flux. The reduction was effected in crucibles or cylinders of fire clay.

Aluminium has also been prepared directly from cryolite by reduction with sodium, but the metal thus obtained is said to be more contaminated with iron and silicon than that prepared by Deville's process. The metal is now obtained by decomposition of the oxide dissolved in a bath of fused cryolite, by means of an electric furnace. Alumina, the only known oxide of aluminium, is not reducible by the action of carbon alone at any attainable furnace temperature, but when alumina mixed with charcoal is heated to the high temperature of the electric arc metallic aluminium separates. Thick rods of gas carbon are used as the poles by which the current for the production of the arc is introduced into the fused mass. Alumina in the form of bauxite is added from time to time in proportion as the metal is reduced. This does not appear to be essentially a process of electrolysis but chiefly a chemical decomposition of alumina by carbon at the high temperature of the electric arc. Carbonic oxide accompanied by fluorine escapes.

Aluminium is remarkable for its low density, which is 2·67; it is nearly as white as silver, and is capable of assuming a high polish. It is employed in the manufacture of delicate apparatus and ornamental articles. Some of the alloys of aluminium are more generally

applicable, more especially the alloy with copper, which is remarkable for being similar in appearance to gold: this alloy is found in commerce under the name of *aluminium bronze.*

The alloys of aluminium with copper are now produced to some extent by a process patented by Messrs E. H. and A. H. Cowles. The apparatus used consists of a firebrick box or furnace, through the end walls of which project two large carbon electrodes connected with a powerful dynamo-machine. The furnace is lined with a mixture of charcoal and lime, and is filled with a mixture of corundum (alumina) with charcoal and granulated copper. On passing the current between the carbon poles aluminium is liberated, and unites with the copper to form an alloy, to which a larger quantity of copper can afterwards be added if desired.

Aluminium forms only one class of compounds, in which it is trivalent, one atom of the metal being equivalent to three atoms of hydrogen; thus the chloride is $AlCl_3$, the oxide, Al_2O_3, etc. These compounds might indeed be represented by formulæ into which the metal enters as a tetrad, *e.g.*, the chloride $Cl_3Al—AlCl_3$, the oxide $O\left\langle\begin{array}{l} Al=O \\ | \\ Al=O \end{array}\right.$, etc., but the simpler formulæ are justified, as already observed (p. 267), by the vapour-density of aluminium chloride, which is in accordance with the formula $AlCl_3$, and by the position of aluminium in Mendelejeff's series.

Aluminium Chloride, $AlCl_3$.—This compound is obtained in solution by dissolving alumina or aluminium hydrate in hydrochloric acid; but the solution, when evaporated, gives off hydrochloric acid and leaves alumina. The anhydrous chloride may be prepared by heating a mixture of alumina and finely divided carbon in chlorine gas.

Pure precipitated alumina is dried and mixed with oil and lampblack, and the mixture, after being strongly calcined in a covered crucible, is introduced into a porcelain tube or tubulated earthen retort, placed in a furnace and connected at one end with an apparatus for evolving chlorine, and at the other with a dry receiver. On raising the heat to bright redness, and passing chlorine through the apparatus, aluminium chloride distils over, together with carbon monoxide, and condenses as a solid mass in the receiver:

$$Al_2O_3 \quad + \quad C_3 \quad + \quad Cl_6 \quad = \quad 2AlCl_3 \quad + \quad 3CO\,.$$

Aluminium chloride is a transparent waxy substance, having a crystalline structure, colourless when pure, but generally exhibiting a yellow colour, due perhaps to the presence of iron. It boils* at about 180°, fumes in the air, and smells of hydrochloric acid. It is very deliquescent, and dissolves readily in water; the solution when

* For a synopsis of all the published determinations of vapour-densities of chlorides of aluminium and allied metals, see a paper by Professor S. Young in *Nature*, Dec. 27, 1888.

left to evaporate yields the hydrated chloride, $AlCl_3,6H_2O$, in six-sided prisms, which when heated are resolved into alumina and hydrochloric acid.

Aluminium and Sodium Chloride, $AlCl_3,NaCl$, is obtained by melting together the component chlorides in proper proportions, or by adding the requisite quantity of sodium chloride to the mixture of alumina and charcoal used for the preparation of aluminium chloride, igniting the mass in chlorine or hydrochloric acid, and condensing the vapour in a receiver. It is a crystalline mass, less deliquescent than aluminium chloride, and, therefore, more convenient for the preparation of aluminium.

Aluminium Fluoride, AlF_3, is produced by the action of gaseous silicon fluoride on aluminium, and forms cubic crystals, volatilising at a red heat, insoluble in water, and resisting the action of all acids.

Aluminium and Sodium Fluoride, $AlF_3,3NaF$, occurs abundantly as cryolite, at Evigtok in Greenland, and is prepared artificially by pouring hydrofluoric acid in excess on a mixture of calcined alumina and sodium carbonate. Cryolite forms quadratic crystals, colourless, transparent, softer than felspar, and of density 2·96. It is used, as already mentioned, for the preparation of aluminium, and in Germany to a small extent for the manufacture of sodium carbonate.

With this object it is heated with chalk whereby calcium fluoride and a soluble sodium aluminate is formed from which the alumina is precipitated by carbon dioxide.

Aluminium Oxide.—Alumina, Al_2O_3.—This substance is prepared by mixing a solution of alum with excess of ammonia, by which an extremely bulky, white, gelatinous precipitate of aluminium hydrate is thrown down. This is washed, dried, and ignited to whiteness. Thus obtained, alumina constitutes a white, tasteless, coherent mass, very little acted upon by acids. It is fusible before the oxyhydrogen blow-pipe. The mineral called *corundum*, of which the ruby and sapphire are transparent varieties, consists of nearly pure alumina in a crystallised state, with a little colouring oxide; emery, used for polishing glass and metals, is a coarse variety of corundum. Alumina imperfectly neutralises acids, and its salts have an acid reaction.

Aluminium Hydrates.—Aluminium forms three hydrates, namely :—

Monohydrate, . . .	Al_2O_3,H_2O or $AlO(OH)$
Dihydrate, . . .	$Al_2O_3,2H_2O$ or $Al_2O(OH)_4$
Trihydrate, . . .	$Al_2O_3,3H_2O$ or $Al(OH)_3$.

The first is found native, as *diaspore*, in translucent masses, which crumble to powder when heated, and give off the whole of their water at 360°.

The third is the ordinary gelatinous precipitate obtained by treating solutions of aluminium salts—alum, for example—with

ammonia or alkaline carbonates. When dried at a moderate heat, it forms a soft friable mass, which adheres to the tongue and forms a stiff paste with water, but does not dissolve in that liquid. At a strong red heat it gives off water, and undergoes a very great contraction of volume. It dissolves with great facility in acids, and in the fixed caustic alkalis. When a solution of alumina in caustic potash is exposed to the air, the potash absorbs carbonic acid, and the aluminium trihydrate is then deposited in white crystals, which are but sparingly soluble in acids.

Aluminium trihydrate has a very powerful attraction for organic matter, and when digested in solutions of vegetable colouring matter, combines with and carries down the colouring matter, which is thus removed entirely from the liquid if the alumina is in sufficient quantity. The pigments called *lakes* are compounds of this nature. The fibre of cotton impregnated with alumina acquires the same power of retaining colouring matters : hence the great use of aluminous salts as *mordants* to produce fast colours.

Aluminium trihydrate occurs native as *gibbsite*, a stalactitic, translucent, fibrous mineral, easily dissolved by acids, occuring at Gumuch-dagh in Asia Minor, at Richmond in Massachusetts, and other localities in the United States ; also as *hydrargyllite*, near Slatoust in the Ural, in small hexagonal prisms.

Dihydrate.—When a dilute solution of aluminium diacetate is exposed for several days to a temperature of 100° in a close vessel, acetic acid appears to be formed, although no precipitation of alumina takes place. The liquid acquires the taste of acetic acid, and if afterwards boiled in an open vessel, gives off nearly the whole of its acetic acid, the alumina, nevertheless, remaining in solution. This solution is coagulated by mineral acids and by most vegetable acids, by alkalis, and by decoctions of dye-woods. The alumina contained in it is, however, no longer capable of acting as a mordant. Its coagulum with dye-woods has the colour of the infusion, but is translucent and totally different from the dense opaque lakes which ordinary alumina forms with the same colouring matters. On evaporating the solution to dryness at 100°, the alumina remains in the form of dihydrate, retaining only a trace of acetic acid. In this state it is insoluble in the stronger acids, but soluble in acetic acid, provided it has not been previously coagulated in the manner just mentioned. Boiling potash converts it into the trihydrate (Crum).

An aluminium dihydrate, called *Bauxite*, in which the aluminium is partly replaced by iron, viz., $(AlFe)_2O_3,2H_2O$ or $(AlFe)_2O(OH)_4$, occurs in roundish masses at Beaux, near Arles, in France, also near Belfast and in other places, and is largely employed for the preparation of alumina and metallic aluminium.

Aluminates.—The hydrogen in aluminium trihydrate may be replaced by an equivalent quantity of various metals ; such compounds are called *aluminates.* According to Frémy, a solution of alumina in potash slowly evaporated out of contact with the air,

deposits granular crystals of potassium aluminate, $AlKO_2$, or $Al_2K_2O_4 = Al_2O_3,K_2O$. Similar compounds occur native: thus *Spinell* is an aluminate of magnesium, Al_2MgO_4; *Gahnite*, an aluminate of zinc, Al_2ZnO_4.

Aluminium Sulphide, Al_2S_3.—When the vapour of carbon bisulphide is passed over alumina at a bright red heat, a glassy melted mass remains, which is instantly decomposed by water, with evolution of sulphuretted hydrogen.

Aluminium Sulphate, $Al_2(SO_4)_3,18H_2O$, or $Al_2O_3,3SO_3,18H_2O$. —Prepared by saturating dilute sulphuric acid with aluminium hydrate, and evaporating; or, on the large scale, by heating clay with sulphuric acid. It crystallises in thin pearly plates, soluble in two parts of water; it has a sweet and astringent taste, and an acid reaction. Heated to redness, it is decomposed, leaving pure alumina.

Aluminium sulphate combines with the sulphates of potassium, sodium, and ammonium, and the other alkali-metals, forming double salts of great interest, the *alums*. Common alum, the source of all the preparations of alumina, contains $AlK(SO_4)_2,12H_2O$. This was formerly manufactured on a very large scale from a kind of slaty clay loaded with iron bisulphide, which abounds on the Yorkshire coast and in Scotland. When this is gently roasted, and then exposed to the air in a moistened state, oxygen is absorbed, ferrous sulphate and aluminium sulphate are produced, and may be afterwards separated by lixiviation with water. The solution, mixed with a quantity of potassium chloride, forms ferrous chloride and potassium sulphate, and the latter combines with the aluminium sulphate to form alum. By crystallisation the alum may be separated from the highly-soluble iron chloride, and afterwards easily purified by a repetition of the process.

Alum is now manufactured by treating alum-clay, bauxite or alunite with sulphuric acid so as to form aluminium sulphate, and converting this salt into crystallised alum by adding potassium chloride or ammonium sulphate to the strong solution.

Potassium-alum crystallises in colourless transparent octahedrons, which often exhibit the faces of the cube. It has a sweetish and astringent taste, reddens litmus paper, and dissolves in 18 parts of water at 15·5°, and in its own weight of boiling water. Exposed to heat, it is easily rendered anhydrous, and by a very high temperature it is decomposed. The crystals have little tendency to change in the air. Alum is largely used in the arts, in preparing skins, dyeing, etc.: it is occasionally contaminated with iron oxide, which interferes with some of its applications. The celebrated Roman alum, made from *alum-stone*, a felspathic rock altered by sulphurous vapours, was once much prized on account of its freedom from this impurity. A mixture of dried alum and sugar, carbonised in an open pan, and then heated to redness in a glass flask, contact with

air being avoided, furnishes *Homberg's pyrophorus*, which ignites spontaneously on exposure to the air. The essential ingredient is, in all probability, finely-divided potassium sulphide.

A process has been patented by Messrs Duncan and Newlands for separating the potash from syrups of beet and cane sugar by means of aluminium sulphate, the potash being thereby precipitated in the form of alum. A solution of aluminium sulphate of a density corresponding with about 27° of Baumé's hydrometer is added to the cold syrup having a density of about 36° B., in quantity sufficient to precipitate the whole of the potash present; the mixture is well stirred for fifteen minutes to an hour; and the whole left at rest for four or five hours till the deposit has completely subsided. This deposit consists of small crystals, technically known as "alum meal." Considerable quantities of alum were a few years ago made by this process.

Sodium-alum, in which sulphate of sodium replaces sulphate of potassium, has a form and constitution similar to that of common alum: it is, however, much more soluble and difficult to crystallise.

Ammonium-alum, containing NH_4 instead of K, very closely resembles common potassium-alum, having the same figure, appearance, and constitution, and nearly the same degree of solubility as that substance. When heated to redness ammonium-alum yields pure alumina.

Cæsium-alum, $AlCs(SO_4)_2,12H_2O$, and
Rubidium alum, $AlRb(SO_4)_2,12H_2O$,
resemble potassium-alum. A *silver alum*, $AlAg(SO_4)_2,12H_2O$, is formed by heating equivalent quantities of argentic and aluminium sulphates till the former is dissolved. It crystallises in regular octahedrons, and is resolved by water into its component salts. There is also a *thallium-alum*, $AlTl(SO_4)_2,12H_2O$, which crystallises in regular octahedrons.

Lastly, there are alums isomorphous with those just described, in which the aluminium is replaced by iron, chromium, and manganese: for example, *potassio-ferric sulphate* or *potassium-iron alum*, $FeK(SO_4)_2,12H_2O$; *ammonio-chromic sulphate*, $Cr(NH_4)(SO_4)_2, 12H_2O$. These will be described further on.

Experiments.—Mix in a beaker not less than about 2 ounces of pipe-clay or alum clay with about twice its weight of oil of vitriol, cover with a clock-glass and heat on sand to near the boiling-point of the acid for two or three hours. Let the mass cool, dilute with about six times its bulk of water, boil and filter. Take a quantity of potassium chloride about equal to that of the clay employed, dissolve it in a small quantity of water, mix the solution with that of the aluminium sulphate just prepared. Stir vigorously till a copious deposit of granular alum is formed. Let this subside, pour off the solution, boil up the powder in seven or eight times its weight of water, and allow it to cool slowly. Large octahedral crystals of alum should be formed in the course of a few hours.

Phosphates.—The *normal salt*, $AlPO_4$ or $Al_2(PO_4)_2$, is obtained on adding a neutral solution of alum to a solution of ordinary sodium phosphate, as a gelatinous precipitate, which dissolves in caustic potash or soda and in mineral acids, but not in ammonia or in acetic acid. On adding ammonia to a solution of this salt in hydrochloric acid, a precipitate is formed, consisting of a basic salt, $3Al_2(PO_4)_2,Al_2(OH)_6+15H_2O$. The mineral *wavellite*, which occurs in trimetric crystals, or in hemispherical or globular concretions having a radiate structure, is likewise a basic aluminium phosphate having the composition $2Al_2(PO_4)_2,Al_2(OH)_6+9H_2O$: it also contains small quantities of fluorine and sometimes of chlorine. *Turquois* is another basic aluminium phosphate, containing $Al_2(PO_4)_2,Al_2(OH)_6+2H_2O$.

Silicates.—Silicates of aluminium enter into the composition of a number of crystallised minerals, among which felspar, by reason of its abundant occurrence, occupies a prominent place. Granite, porphyry, trachyte, and other ancient unstratified rocks, consist in great part of this mineral, which, under particular circumstances, by no means well understood, and particularly by the action of the carbonic acid of the air, suffers complete decomposition, being converted into a soft friable mass of earthy matter. This is the origin of clay: the change itself is seen in great perfection in certain districts of Devonshire and Cornwall, the felspar of the fine white granite of those localities being often disintegrated to a great depth, and the rock altered to a substance resembling soft mortar. By washing, this finely-divided substance is separated from the quartz and mica; and the milk-like liquid, being stored up in tanks, deposits the suspended clay, which is afterwards dried, first in the air, and afterwards in a stove, and employed in the manufacture of porcelain. The composition assigned to unaltered felspar is $AlKSi_3O_8$, or $AlKSiO_4,2SiO_2$, or $Al_2O_3,K_2O,6SiO_2$. The nature of the change by which felspar passes into porcelain clay is not exactly understood, but it consists essentially in the abstraction of silica and alkali.

When the decomposing rock contains iron oxide, the clay produced is coloured. The different varieties of shale and slate result from the alteration of ancient clay-beds, apparently in many instances by the infiltration of water holding silica in solution: the dark appearance of some of these deposits is due to bituminous matter. Clays containing an admixture of calcium carbonate are called *marls*, and may be recognised by their property of effervescing with acids. Pure clays are but little affected by dilute acids, but on boiling them with strong sulphuric acid, alumina is dissolved out and finely-divided silica left behind.

A basic aluminium silicate, Al_2O_3,SiO_2, is found crystallised, constituting the beautiful mineral called *cyanite*. The compounds formed by the union of the aluminium silicates with other silicates

are almost innumerable. A sodium felspar, *albite*, containing that metal in place of potassium, is known, and there are two somewhat similar lithium compounds, *spodumene* and *petalite*. The *zeolites* are hydrated silicates belonging to this class; *analcime*, *nepheline*, *mesotype*, etc., are double silicates of sodium and aluminium, with water of crystallisation. *Stilbite*, *heulandite*, *laumontite*, *prehnite*, etc., consist of calcium silicate combined with silicate of aluminium. The *garnets*, *axinite*, *mica*, etc., have a similar composition, but are anhydrous. Iron sesquioxide is very often substituted for alumina in these minerals.

Reactions of Aluminium Salts.—Alumina and salts of aluminium, when moistened with *cobalt nitrate* and heated before the blow-pipe, assume a characteristic blue colour.

Alumina when in solution is readily distinguished. Caustic *potash* and *soda* occasion a white gelatinous precipitate of aluminium hydrate, freely soluble in excess of the alkali. *Ammonia* produces a similar precipitate, insoluble in excess of the reagent. The *alkaline carbonates* and *carbonate of ammonia* precipitate the hydrate, with escape of carbonic acid. The precipitates are insoluble in excess.

Ammonium sulphide also produces a white precipitate of aluminium hydrate.

Porcelain and Earthenware.—The plasticity of natural clays, and their hardening when exposed to heat, are properties which suggested in very early times their application to the making of vessels for the various purposes of daily life: there are few branches of industry of higher antiquity than that exercised by the potter.

True porcelain is distinguished from earthenware by very obvious characters. In porcelain the body of the ware is very compact and translucent, and breaks with a conchoïdal fracture, indicative of incipient fusion. The glaze, too, applied for giving a perfectly smooth surface, is closely adherent, and, in fact, graduates by insensible degrees into the substance of the porcelain. In earthenware, on the contrary, the fracture is open and earthy, and the glaze may be detached with greater or less facility. The compact and partly glassy character of porcelain is the result of the admixture with the clay of a small portion of some substance, such as felspar, or a calcic or alkaline silicate, which is fusible at the temperature to which the ware is exposed when baked or fired, and being absorbed by the less-fusible portion, binds the whole into a solid mass on cooling. The clay employed in porcelain-making is always directly derived from decomposed felspar, none of the clays of the secondary strata being pure enough for the purpose: it must be white, and free from iron oxide. To diminish the contraction which this substance undergoes in the fire, a quantity of finely-divided silica, carefully prepared by crushing and grinding calcined flints or chert, is added,

together with a proper proportion of felspar or other fusible material, also reduced to impalpable powder. The utmost pains are taken to effect perfect uniformity of mixture, and to avoid the introduction of particles of grit, or other foreign bodies. The ware itself is fashioned either on the potter's wheel—a kind of vertical lathe—or in moulds of plaster of Paris, and dried first in the air, afterwards by artificial heat, and at length completely hardened by exposure to the temperature of ignition. The porous *biscuit* is now fit to receive its glaze, which may be either ground felspar or a mixture of gypsum, silica, and a little porcelain clay, diffused through water. The piece is dipped for a moment into this mixtnre, and withdrawn ; the water sinks into its substance, and the powder remains evenly spread upon its surface ; it is once more dried, and, lastly, fired at an exceedingly high temperature.

The porcelain-furnace is a circular structure of masonry, having several fire-places, and surmounted by a lofty dome. Dry wood or coal is consumed as fuel, and its flame is directed into the interior, and made to circulate around and among the earthen cases, or *seggars*, in which the articles to be fired are packed. Many hours are required for this operation, which must be very carefully managed. After the lapse of several days, when the furnace has completely cooled, the contents are removed in a finished state, so far as regards the ware.

The ornamental part, consisting of gilding and painting in enamel, has yet to be executed ; after which the pieces are again heated, in order to flux the colours. The operation has sometimes to be repeated more than once.

The manufacture of porcelain in Europe is of modern origin ; the Chinese have possessed the art from the commencement of the seventh century, and their ware is, in some respects, altogether unequalled. The materials employed by them are known to be *kaolin* or decomposed felspar : *petuntze*, or quartz reduced to fine powder ; and the ashes of fern, which contain potassium carbonate.

Stoneware.—This is a coarse kind of porcelain, made from clay containing oxide of iron and a little lime, to which it owes its partial fusibility. The glazing is performed by throwing common salt into the heated furnace ; this is volatilised, and decomposed by the joint agency of the silica of the ware and of the vapour of water always present ; hydrochloric acid and soda are produced, the latter forming a silicate, which fuses over the surface of the ware, and gives a thin but excellent glaze.

Earthenware.—The finest kind of earthenware is made from a white secondary clay, mixed with a considerable quantity of silica. The articles are thoroughly dried and fired ; after which they are dipped into a readily-fusible glaze mixture, of which lead oxide is usually an important ingredient, and when dry, reheated to the melting-point of the latter. The whole process is much easier of execution than the making of porcelain, and demands less care. The ornamental designs in blue and other colours, so common upon plates and

household articles, are printed upon paper in enamel pigment mixed with oil, and transferred, while still wet, to the unglazed ware. When the ink becomes dry, the paper is washed off, and the glazing completed.

The coarser kinds of earthenware are sometimes covered with a whitish opaque glaze, which contains the oxides of lead and tin; such glaze is very liable to be attacked by acids, and is dangerous for culinary vessels.

Crucibles, when of good quality, are very valuable to the chemist. They are made of clay free from lime, mixed with sand or ground ware of the same description. The Hessian and Cornish crucibles are among the best. Sometimes a mixture of plumbago and clay is employed for the same purpose; and powdered coke has been also used with the earth: such crucibles bear rapid changes of temperature with impunity.

GALLIUM.

Symbol, Ga. Atomic weight, 70.

This metal was discovered in 1875 by Lecoq de Boisbaudran, in a zinc-blende from the mine of Pierrefitte, in the valley of Argeles, Pyrenees, and has likewise been found, although always in very small quantity, in blendes from other localities. It is separated by dissolving the blende in nitromuriatic acid, immersing plates of zinc in the solution till the disengagement of hydrogen becomes slow—whereby copper, lead, cadmium, and other metals are precipitated—and then boiling the clear liquid for several hours with a large excess of zinc, which throws down alumina, basic zinc-salts, and oxide of gallium. This precipitate is redissolved in hydrochloric acid; the solution again boiled with zinc; the resulting precipitate, which contains the gallium in a more concentrated form, is redissolved in hydrochloric acid; the solution mixed with ammonium acetate is treated with hydrogen sulphide, which throws down the zinc and gallium as sulphides, leaving the aluminium in solution; and this treatment is repeated to ensure the complete separation of the alumina. The white sulphides of zinc and gallium are then dissolved in hydrochloric acid; the solution is fractionally precipitated with sodium carbonate, the gallium going down chiefly in the first portions; and, to complete the separation of the zinc, the gallium oxide is dissolved in sulphuric acid and reprecipitated by excess of ammonia; this dissolves all the zinc oxide, and the greater part of the gallium oxide, which may be reprecipitated by boiling the liquid to expel the free ammonia.

Metallic gallium is obtained by electrolysing a solution of the oxide in potash or ammonia with platinum electrodes, the gallium being deposited on the negative plate as a compact, closely-adhering crust, which may be detached by bending the plate backwards and forwards under cold water.

Gallium is a hard metal somewhat whiter than platinum, and acquires a good polish by pressure ; it is sectile and somewhat malleable ; its density is 5·9, which is intermediate between that of aluminium (2·7) and that of indium (7·4). Its melting-point is 30·1°, so that it liquefies when pressed between the fingers ; frequently also it remains liquid for a long time even when cooled nearly to 0°. The melted metal adheres to glass, forming a mirror whiter than that produced by mercury. When heated to bright redness in contact with the air, it oxidises merely on the surface, and does not volatilise.

Gallium forms a very bright electric spectrum, exhibiting a brilliant line and a fainter band in the violet. In a gas-flame only the line is exhibited, and even this is very faint and fugitive. It was by these spectroscopic characters that the existence of gallium was first recognised.

Gallium chloride is very soluble and deliquescent. Its aqueous solution is clear when highly concentrated, but becomes turbid on addition of water ; the precipitate (probably an oxychloride) dissolves but very slowly in hydrochloric acid. A slightly acidulated solution of the chloride evaporated at a gentle heat, deposits needles which act strongly on polarised light. The *sulphate* is not deliquescent.

Gallium forms an *ammonia-alum*, which crystallises in octahedrons like common alum ; it dissolves in cold water, but the solution becomes turbid on boiling, and is decomposed by heating with acetic acid. The existence of this alum shows that the oxide of gallium is represented by the formula Ga_2O_3, and its chloride by $GaCl_3$.

Solutions of gallium salts give with *ammonium sulphide* a white precipitate of gallium sulphide insoluble in excess of the reagent. The same precipitate is formed by *hydrogen sulphide* in presence of acetic, but not of hydrochloric acid. *Ammonia* and *carbonate of ammonia* give white precipitates soluble in excess. Slightly acid solutions of the chloride and sulphate are not precipitated in the cold by *ammonium acetate;* but the neutral solutions are clouded thereby. Gallium oxide is easily precipitated by *barium carbonate*, *cupric hydroxide*, and *potassium ferrocyanide*, the last-mentioned reagent affording an extremely delicate test of its presence.

In a mixed solution of gallium and aluminium, the latter is precipitated before the gallium, and in a mixed solution of gallium and indium, the gallium goes down first ; in point of basicity, therefore, gallium is intermediate between aluminium and indium.

The existence of a metal having the atomic weight and properties of gallium was predicted, as already observed, by Mendelejeff (p. 271).

INDIUM.

Symbol, In. Atomic Weight, 113.

This metal was first discovered in 1863 by Reich and Richter, in the zinc-blende of Freiberg, and has since been found in a few other

zinc-ores and in the flue-dust of zinc furnaces. The metallic sponge which remains when the crude zinc of the Freiberg works is dissolved in dilute sulphuric acid, contains the whole of the indium (0·045 per cent.), together with lead, arsenic, cadmium, and iron. It is dissolved in nitric acid; the lead, arsenic, and cadmium are precipitated by hydrogen sulphide; and the filtered solution is heated with potassium chlorate to bring all the iron to the state of ferric salt, and then treated with ammonia, which precipitates the indium as a hydroxide, together with iron and zinc. The precipitate is dissolved in acetic acid; and the indium, precipitated as sulphide by hydrogen sulphide, is freed from traces of iron and zinc by dissolving the precipitate in dilute hydrochloric acid, precipitating the indium by agitation with barium carbonate, dissolving out the indium hydroxide by dilute sulphuric acid, and reprecipitating with ammonia.

Indium, reduced from its oxide by ignition with sodium, is a silver-white metal, soft and ductile, has a density of 7·421, melts at 176°, and is less volatile than cadmium or zinc. When heated to redness in the air, it burns with a violet flame, and is converted into the yellow sesquioxide. Heated in chlorine, it burns with a yellow-green light, and forms a chloride, which sublimes without fusion at an incipient red heat, in soft white laminæ.

Indium dissolves in the strong mineral acids, and is precipitated from the solutions by *zinc* and *cadmium*. *Hydrogen sulphide* precipitates it completely, as a yellow sulphide, from a solution of its acetate, and from neutral solutions of indium salts in general, but not from solutions containing excess of the strong mineral acids. *Ammonia* and *sodium carbonate* produce white precipitates insoluble in excess: *caustic potash* or *soda* throws down white indium hydroxide soluble in excess of the alkali. *Ammonium carbonate* forms a white precipitate soluble in excess, and reprecipitated on boiling. *Barium carbonate* precipitates indium completely.

The spectrum of indium is characterised by two indigo-coloured lines, one very bright and more refrangible than the blue line of strontium, the other fainter and still more refrangible, and approaching the blue line of potassium. It was the observation of this peculiar spectrum that led to the discovery of the metal.

The formulæ of the principal normal indium compounds are as follows:—

Chloride, ...	$InCl_3$
Indium and ammonium chloride, .	$2NH_4Cl,InCl_3+H_2O$
Yellow oxide, ...	In_2O_3
Hydroxide, ...	InH_3O_3
Nitrate, ...	$In(NO_3)_3$
Sulphate, ...	$In_2(SO_4)_3+9H_2O$.

The yellow oxide, heated in a stream of hydrogen, is successively reduced to a green, a grey, and a black oxide, and at a low red heat to the metallic state.

METALS OF THE IRON GROUP.

Manganese.	Cobalt.
Iron.	Nickel.

These are metals of very high melting-point, and are all attracted more or less by a magnet. Manganese and iron are somewhat readily oxidised when heated in air or steam, but cobalt and nickel decompose steam only slowly, and attack hydrochloric and dilute sulphuric acid feebly. They all combine with small quantities of carbon and of silicon, forming alloys which are harder and more fusible than the pure metals.

These metals form oxides, MO, in which they are bivalent, and corresponding sulphates, which unite with the sulphates of the alkali-metals, forming double sulphates isomorphous with those of the magnesium group, *e.g.*, $K_2Fe(SO_4)_2+6H_2O$. Manganese and iron also form sesquioxides, M_2O_3, and the corresponding sulphates, which, like aluminium sulphate, unite with sulphates of alkali-metals forming *alums* isomorphous with common alum ; *e.g.*, *potassio-ferric sulphate*, $KFe'''(SO_4)_2 + 12H_2O$, or $K_2(Fe_2)^{vi}(SO_4)_4+24H_2O$. The corresponding salts of nickel and cobalt are very unstable, and hence the sesquioxides of these metals dissolve in acids with evolution of oxygen or chlorine. Manganese and iron likewise form salts which may be supposed to contain the trioxides MO_3, or in which the metal is sexvalent, analogous therefore in composition to the sulphates, *e.g.*, *potassium ferrate*, K_2FeO_4 or K_2O,FeO_3. Lastly, manganese forms a class of salts, the *permanganates*, *e.g.*, $KMnO_4$ or K_2O,Mn_2O_7, analogous in composition to the perchlorates, and isomorphous therewith.

The valence of manganese has already been considered (pp. 269, 270).

MANGANESE.

Symbol, Mn. Atomic weight, 54.

Manganese is tolerably abundant in nature in the state of oxide, occurring chiefly as dioxide or pyrolusite, MnO_2 ; also as braunite, Mn_2O_3, and hausmannite, Mn_3O_4 ; and as carbonate in rhodochrosite or manganese spar, $MnCO_3$, which also occurs frequently as an isomorphous constituent in ferrous carbonate and other similar minerals. Manganese likewise enters, though only in small quantity, into the composition of many other minerals, and traces of it, derived from the soil, are often found in the ashes of plants.

Metallic manganese, or perhaps strictly, manganese carbonide, may

be prepared by reducing the oxide with charcoal at a white heat. The metal may also be obtained by heating the anhydrous chloride with magnesium.

Manganese is very hard and brittle, and, when powdered, decomposes water, even at the lowest temperature. Dilute sulphuric acid dissolves it with great energy, evolving hydrogen.

Alloys of iron with relatively large quantities of manganese and 4 or 5 per cent. of carbon are now manufactured by reducing in the blast-furnace (p. 478) the native carbonate or oxide. "Spiegeleisen," or mirror iron, is a name applied to one of these, the broken surface of which exhibits large crystalline faces. It may be regarded as a kind of cast iron in which 15 to 20 or 25 per cent. of the iron is replaced by manganese. Ferro-manganese is another mixture sometimes containing 80 to 90 per cent. of manganese. These manganiferous alloys are extensively used in steel-making.

Manganese Chlorides.—*Manganous Chloride*, $MnCl_2$, may be prepared in a state of purity from the dark-brown liquid residue of the preparation of chloride from manganese dioxide and hydrochloric acid, which often accumulates in the laboratory to a considerable extent; from the pure chloride, the carbonate and all the other salts can be conveniently obtained.

Experiment.—The liquid referred to consists chiefly of the mixed chlorides of manganese and iron: it is filtered, evaporated to perfect dryness, and the residue is slowly heated to dull redness in an open vessel, with constant stirring. The iron chloride is thus either volatilised, or converted by the remaining water into insoluble sesquioxide, while the manganese salt is unaffected. On treating the greyish-looking powder thus obtained with water, the manganese chloride is dissolved out, and may be separated by filtration from the iron oxide. Should a trace of the latter yet remain, it may be got rid of by boiling the liquid for a few minutes with a little manganese carbonate. The solution of the chloride has usually a delicate pink colour, which becomes very manifest when the salt is evaporated to dryness. A strong solution deposits rose-coloured tabular crystals, which contain 4 molecules of water; they are very soluble and deliquescent. The chloride is fusible at a red heat, is decomposed slightly at that temperature by contact with air, and is dissolved by alcohol, with which it forms a crystallisable compound.

Manganic Chloride, Mn_2Cl_6, is formed when precipitated manganic oxide is immersed in cold concentrated hydrochloric acid, the oxide then dissolving quietly without evolution of gas. Heat decomposes the solution, yielding manganous chloride and free chlorine.

The *Tetrachloride*, $MnCl_4$, is formed when manganese dioxide is dissolved in hydrochloric acid. It is said to yield a green solution in ether, but it is very easily resolved into manganous chloride and free chlorine.

Oxychloride, MnO_2Cl_2(?).—When potassium permanganate is dis-

solved in strong sulphuric acid, and fused sodium chloride is added by small portions at a time, a greenish-yellow gas is given off, which condenses at 0° to a greenish-brown liquid. This compound, when exposed to moist air, gives off fumes, coloured purple by permanganic acid, and is instantly decomposed by water into permanganic and hydrochloric acids.

Manganese Oxides.—Manganese forms five distinct oxides, as follows :—

Monoxide, or Manganous oxide, ...	MnO
Trimangano-tetroxide, or Manganoso-manganic oxide,	Mn_3O_4
Sesquioxide, or Manganic oxide, ...	Mn_2O_3
Dioxide or Peroxide, ...	MnO_2
Trioxide, ...	MnO_3.

The first and third of these are the salifiable oxides of manganese. The second may be regarded as a compound of the first and third, MnO,Mn_2O_3 ; there are also several oxides intermediate between the monoxide and dioxide, occurring as natural minerals or ores of manganese. Manganese likewise forms two series of oxygen-salts, called *manganates* and *permanganates*, the composition of which has been already noticed. The trioxide is the anhydride of manganic acid.

Monoxide, or *Manganous Oxide*, MnO.—When manganese carbonate is heated in a stream of hydrogen gas, or vapour of water, carbon dioxide is disengaged, and a greenish powder left behind, which is the monoxide. Prepared at a dull-red heat only, the monoxide is so prone to absorb oxygen from the air, that it cannot be removed from the tube without change ; but when prepared at a higher temperature, it appears more stable. This oxide dissolves quietly in dilute acids, neutralising them completely, and forming salts, which have often a beautiful pink colour, and are isomorphous with salts of magnesium and zinc. When alkalis are added to solutions of these compounds, the white hydrate first precipitated speedily becomes brown by passing into a higher state of oxidation.

Sesquioxide, or *Manganic Oxide*, Mn_2O_3.—This compound occurs in nature as *braunite*, and in the state of hydrate as *manganite:* a very beautiful crystallised variety is found at Ilefeld, in the Hartz. It is produced artificially, by exposing the hydrated monoxide to the air, and forms the principal part of the residue left in the iron retort when oxygen gas is prepared by exposing the native dioxide to a moderate red heat. The colour of the sesquioxide is brown or black, according to its origin or mode of preparation. It is isomorphous with alumina : for when gently heated with diluted sulphuric acid, it dissolves to a red liquid, which, on the addition of potassium or ammonium sulphate, deposits octahedral crystals having a constitution similar to that of common alum ; these are, however, decomposed by water. On heating this oxide with hydrochloric acid, chlorine is evolved, as with the dioxide, but in smaller amount.

Dioxide, Peroxide of Manganese, MnO_2.—Pyrolusite, the most valuable ore of manganese, is found both massive and crystallised. It may be obtained artificially in the anhydrous state by gently calcining the nitrate; or in combination with water, by adding solution of bleaching-powder to a salt of the monoxide. Manganese dioxide has a black colour, and is insoluble in water. It is decomposed by hot hydrochloric acid and by oil of vitriol with evolution of chlorine and of oxygen respectively. It unites with the alkaline oxides, potash, lime, etc., forming salts called manganites, the most important of which is the manganite of calcium, $CaO.MnO_2$ or $CaMnO_3$, formed in Weldon's process for the recovery of manganese dioxide from waste chlorine-liquors. The waste liquor obtained in the chlorine manufacture consists of a solution of manganous chloride, $MnCl_2$, mixed with ferric chloride, Fe_2Cl_6. The latter is removed in the form of hydrated oxide by neutralising the liquid with chalk. In order to recover the manganese in a form in which it may be again available for the production of chlorine, the clear solution drawn off from the precipitated peroxide of iron, alumina, etc., is mixed with milk of lime, in slight excess, the temperature slightly raised, and air is blown through the mixture till the precipitate becomes black. This is then allowed to settle and is run back into the chlorine stills in the form of a thin mud.

The proportion of real dioxide contained in a commercial sample of the black oxide may be estimated by determining the quantity of carbon dioxide evolved on gently heating a weighed quantity of oxalic acid, $C_2H_2O_4 \cdot 2H_2O$, with strong hydrochloric acid in presence of a known weight of the manganese ore. The following reaction then takes place:

$$MnO_2 + C_2H_2O_4 + 2HCl = MnCl_2 + 2H_2O + 2CO_2.$$

This equation shows that every two molecules of carbon dioxide evolved correspond with one molecule of manganese dioxide decomposed. Now the molecular weight of this oxide, 87, is so nearly equal to twice that of carbon dioxide, 44, that the loss of weight suffered by the apparatus when the reaction has become complete, and the residual gas has been driven off by momentary ebullition, may be taken to represent the quantity of real dioxide in the weight of the sample taken for analysis. Geissler's apparatus (p. 207) may be advantageously used in this process.

Trimangano-tetroxide, or *Red Manganese Oxide*, Mn_3O_4, or MnO,Mn_2O_3.—This oxide is also found native, as *hausmannite*, and is produced artificially by heating the dioxide or sesquioxide to whiteness, or by exposing the monoxide or carbonate to a red heat in an open vessel. It is a reddish-brown substance, incapable of forming salts, and acted upon by acids in the same manner as the two other oxides already described. Borax and glass in the fused state dissolve it, and acquire the colour of amethyst.

Varvicite, Mn_4O_7,H_2O or $MnO,3MnO_2,H_2O$, is a natural mineral discovered by Phillips among certain specimens of manganese ore

from Warwickshire: it has also been found at Ilefeld in the Hartz. It much resembles the dioxide, but is harder and more brilliant. By a strong heat, varvieite is converted into red oxide, with disengagement of aqueous vapour and oxygen gas.

Several other oxides intermediate in composition between the monoxide and dioxide, also occur native; they are probably mere mixtures, and in many cases the monoxide is more or less replaced by the corresponding oxides of iron, cobalt, and copper.

The *Trioxide*, MnO_3, has been obtained in small quantity by dissolving potassium permanganate in concentrated sulphuric acid, and allowing the solution to fall drop by drop upon dry sodium carbonate placed in a flask. Red clouds are formed, which, on passing through a tube filled with broken glass and cooled by a freezing mixture, condense to a red deliquescent solid. The formation of the trioxide is supposed to take place according to the following equation, oxygen and carbon dioxide gases escaping:

$$(MnO_3)_2SO_4 + Na_2CO_3 = Na_2SO_4 + 2MnO_3 + CO_2 + O.$$

The trioxide is decomposed by water with formation of permanganic acid and manganese dioxide:

$$3MnO_3 + H_2O = 2HMnO_4 + MnO_2.$$

(Thorpe and Hambly, 1888.)

Oxysalts of Manganese.—*Manganous Sulphate*, $MnSO_4,7H_2O$ or $MnO,SO_3,7H_2O$.—A beautiful rose-coloured and very soluble salt, isomorphous with magnesium sulphate. It is prepared on the large scale for the use of the dyer, by heating in a close vessel manganese dioxide and coal, and dissolving the impure monoxide thus obtained in sulphuric acid, with addition of a little hydrochloric acid towards the end of the process. The solution is evaporated to dryness, and again exposed to a red heat, by which ferric sulphate is decomposed. Water then dissolves out the pure manganese sulphate, leaving ferric oxide behind. This salt is used to produce a permanent brown dye, the cloth steeped in the solution being afterwards passed through a solution of bleaching-powder, by which the monoxide is changed to insoluble hydrated dioxide. Manganous sulphate sometimes crystallises with 5 molecules of water. It forms a double salt with potassium sulphate, containing $MnK_2(SO_4)_2,6H_2O$.

Manganous Carbonate, $MnCO_3$.—Prepared by precipitating the dichloride with an alkaline carbonate. It is an insoluble white powder, sometimes with a buff-coloured tint. Exposed to heat, it loses carbon dioxide and absorbs oxygen.

Manganates.—When an oxide of manganese is fused with potash, oxygen is taken up from the air, and a deep-green saline mass results, which contains *potassium manganate*, K_2MnO_4. The addition of potassium nitrate or chlorate facilitates the reaction. Water dissolves this compound very readily, and the solution, concentrated by

evaporation in a vacuum, yields green crystals. *Barium manganate*, $BaMnO_4$, is formed in a similar manner. In these salts manganese is probably sexvalent, like chromium in the chromates.

All the manganates are very unstable, being deoxidised by contact with all sorts of organic matter and decomposed by acids, even by carbonic acid.

Permanganates.—When potassium manganate, free from any great excess of alkali, is put into a large quantity of water, it is resolved into hydrated manganese dioxide, which subsides, and *potassium permanganate*, $K_2Mn_2O_8$ or K_2O,Mn_2O_7, which remains in solution, forming a deep-purple liquid :

$$3K_2MnO_4 + 2H_2O = MnO_2 + K_2Mn_2O_8 + 4KHO.$$

This effect is accelerated by heat. The curious changes of colour accompanying this decomposition procured for the manganate the name *mineral chameleon ;* excess of alkali hinders the reaction in some measure, by conferring greater stability on the manganate. Potassium permanganate is easily prepared on a considerable scale. Equal parts of very finely powdered manganese dioxide and potassium chlorate are mixed with rather more than 1 part of potassium hydroxide dissolved in a little water, and the whole is exposed, after evaporation to dryness, to a temperature just short of ignition. The mass is treated with hot water, the insoluble oxide separated by decantation, and the deep-purple liquid concentrated by heat, until crystals form upon its surface : it is then left to cool. The crystals have a dark-purple colour, and are not very soluble in cold water. The manganates and permanganates are decomposed by contact with organic matter. The green and red disinfecting agents, known as Condy's fluids, are alkaline manganates and permanganates.

Hydrogen Permanganate, or *Permanganic Acid*, $H_2Mn_2O_8$, or more probably permanganic anhydride, Mn_2O_7 is obtained by dissolving potassium permanganate in hydrogen sulphate, H_2SO_4, diluted with 1 molecule of water, and distilling the solution at 60°–70°. Permanganic acid then passes over in violet vapours, and condenses to a greenish-black liquid, which has a metallic lustre, absorbs moisture greedily from the air, and acts as a most powerful oxidising agent, instantly setting fire to paper and to alcohol.

Reactions of Manganous Salts.—The *fixed caustic alkalis* and *ammonia* give white precipitates, insoluble in excess, quickly becoming brown. Potassium and sodium *carbonates* and ammonium *carbonate* give white precipitates, but little subject to change, and insoluble in excess of ammonium carbonate. *Hydrogen sulphide* gives no precipitate, but *ammonium sulphide* throws down insoluble flesh-coloured sulphide of manganese, which is very characteristic. *Potassium ferrocyanide* gives a white precipitate.

An excellent and characteristic test for small quantities of manganese is based upon the production of permanganic acid : the solution to be tested is mixed with strong nitric acid and boiled with a little red lead. If manganese is present a *pink colour* will be seen in the solution after the precipitate has subsided.

Manganese is also easily detected by the blow-pipe : it gives with borax an amethyst-coloured bead in the outer or oxidising flame, and a colourless bead in the inner flame. Heated upon platinum foil with sodium carbonate, it yields a green mass of sodium manganate.

IRON.

Symbol, Fe (Ferrum). Atomic weight, 56.

This is the most important of all the metals : there are few substances to which it yields in interest, when we consider how very intimately the knowledge of its properties and uses is connected with human civilisation.

Metallic iron occurs but rarely on the earth, being found only in minute quantity in basalts and other volcanic rocks. It also enters into the composition of many *meteorites*. Isolated masses of soft malleable iron also, of large dimensions, lie loose upon the surface of the earth in South America, Greenland, and elsewhere, and are by some presumed to have had a similar origin : these latter in common with the iron of the undoubted meteorites, contain nickel. In the state of oxide, the presence of iron may be said to be universal : it constitutes a great part of the common colouring matter of rocks and soils : it is contained in plants, and forms an essential component of the blood of the animal body. It is also very common in the state of bisulphide or iron pyrites.

Pure iron may be prepared, according to Mitscherlich, by introducing into a Hessian crucible 4 parts of fine iron wire cut small, and 1 part of black iron oxide. This is covered with a mixture of white sand, lime, and potassium carbonate, in the proportions used for glass-making, and a cover being closely applied, the crucible is exposed to a very high temperature. A button of pure metal is thus obtained, the traces of carbon and silicon present in the wire having been removed by the oxygen of the oxide.

Pure iron has a white colour and perfect lustre : it is extremely soft and tough, and has a density 7·8. Its crystalline form is probably the cube, to judge from appearances occasionally exhibited. In good bar-iron or wire, a distinct fibrous texture may always be observed when the metal has been attacked by rusting or by the application of an acid ; and upon the perfection of this fibre much of its strength is supposed to depend. Iron is the most tenacious of all the metals, a wire $\frac{1}{10}$ of an inch in diameter bearing a weight of 60 lbs. It is very difficult of fusion, and before becoming liquid

passes through a soft or pasty condition. Pieces of iron, pressed or hammered together in this state, cohere into a single mass: this operation, termed *welding*, is usually performed by sprinkling a little sand over the heated metal, which combines with the superficial film of oxide, forming a fusible silicate, which is subsequently forced out from between the pieces of iron by the pressure applied: clean surfaces of metal are thus presented to each other, and union takes place without difficulty.

Iron does not oxidise in dry air at common temperatures; heated to redness, it becomes covered with a scaly coating of black oxide, and at a white heat burns brilliantly, producing the same substance. In oxygen gas the combustion occurs with still greater ease. The finely-divided spongy metal prepared by reducing the red oxide with hydrogen gas, takes fire spontaneously in the air. Pure water, free from air and carbonic acid, does not tarnish a surface of polished iron, but the combined agency of free oxygen and moisture speedily leads to the production of rust, which is a hydrate of the sesquioxide. The rusting of iron is wonderfully promoted by the presence of a little acid vapour. At a red heat, iron decomposes water, evolving hydrogen, and passing into the black oxide. Dilute sulphuric and hydrochloric acids dissolve it freely, with separation of hydrogen. Iron is strongly magnetic up to a red heat, but at that temperature it loses all traces of magnetism.

Iron forms two classes of compounds: namely, the ferrous compounds, and the ferric compounds, in which, like aluminium, it may be regarded either as a triad or a tetrad: ferric chloride, for example, may be either $FeCl_3$ or Fe_2Cl_6; the vapour-density of this compound, as determined by Deville, is in favour of the latter formula. The lower vapour-density, observed more recently by Grünewald and Meyer, was attended by evolution of chlorine. It remains at present doubtful whether ferric chloride is dissociated like aluminium chloride.

The ferrous compounds are usually represented for the sake of simplicity by the formulæ FeO, $FeCl_2$, $FeSO_4$, etc., in which the metal is bivalent; but from Meyer's experiments on the vapour-density of ferrous chloride there can be little doubt that the molecule at low temperatures contains Fe_2Cl_4.

Chlorides.—*Ferrous Chloride*, Fe_2Cl_4 or $FeCl_2$, is formed by transmitting dry hydrochloric acid gas over red-hot metallic iron, or by dissolving iron in hydrochloric acid. The latter solution yields, when duly concentrated, green crystals of the hydrated chloride, $FeCl_2,4H_2O$; they are very soluble and deliquescent, and oxidise rapidly in the air.

Ferric Chloride, Fe_2Cl_6 or $FeCl_3$, may be prepared by dissolving ferric oxide in hydrochloric acid. The solution, evaporated to a syrupy consistence, deposits red hydrated crystals, which are very soluble in water and alcohol. It forms double salts with potassium chloride and sal-ammoniac. When evaporated to dryness and

strongly heated, much of the chloride is decomposed, yielding sesquioxide and hydrochloric acid: the remainder sublimes, and afterwards condenses in the form of small brilliant dark-green crystals, which deliquesce in the air rapidly. Anhydrous ferric chloride is also produced by the action of chlorine upon the heated metal. The solution of ferric chloride is capable of dissolving a large excess of recently precipitated ferric hydroxide, by which it acquires a much darker colour.

Experiments.—1. Fit up the apparatus (p. 95) for the preparation of chlorine, adapt to the tube by which the gas is carried off a small Woulff bottle containing a half-inch stratum of oil of vitriol, and to this bottle fit a piece of "combustion" tube 8 or 10 inches long. Place in the tube, near its connection with the chlorine apparatus, a coil of thin iron wire. Now generate a pretty rapid stream of chlorine in the usual manner, and at the same time heat the wire by means of a Bunsen flame. As soon as pure chlorine begins to pass through the iron will become red-hot, and will yield a dark-green sublimate of ferric chloride, which will be deposited in the cool part of the tube. The experiment must be made in a draught chamber. When the iron is completely converted, the chloride may be dissolved in water and the yellow solution kept for use.

2. Dissolve, with the aid of heat, about 10 grams of iron wire in 30 c.c. of strong hydrochloric acid, diluted with a little water placed in a flask. Pour off half the solution into a dish, and evaporate rapidly till the liquid is reduced to about a third. Pour the strong solution into a beaker, and cover it to exclude the air. Green crystals of ferrous chloride will be deposited.

3. Add to the remainder of the solution of ferrous chloride a little more hydrochloric acid, heat it to boiling, and drop in a small quantity of nitric acid, added *drop by drop*, till dark coloration is no longer observed, and the effervescence ceases. Evaporate the resulting solution to a syrupy consistence, and leave it to cool. Crystals of hydrated ferric chloride, $Fe_2Cl_6.6H_2O$, will be formed.

4. To a portion of the solution of ferrous chloride add excess of solution of ammonia. A pale-green precipitate of ferrous hydroxide is formed, which rapidly darkens and becomes rusty on exposure to air.

5. To a portion of the ferric chloride solution add excess of ammonia. A brown precipitate of ferric hydroxide results.

Iodides.—*Ferrous Iodide*, Fe_2I_4 or FeI_2, is an important medicinal preparation: it is easily made by digesting iodine with water and metallic iron. The solution is pale-green, and yields, on evaporation, crystals resembling those of the chloride, which rapidly oxidise on exposure to air. It is best preserved in solution in contact with excess of iron.—*Ferric Iodide*, Fe_2I_6, is known only in the yellowish-red solution.

Iron Oxides and Oxysalts.—Three oxides of iron are known, namely, ferrous oxide, FeO, and ferric oxide, Fe_2O_3, ana-

logous to the chlorides, and an intermediate oxide, usually called magnetic iron oxide, containing Fe_3O_4 or $FeO{\cdot}Fe_2O_3$. A trioxide, FeO_3, may be supposed to exist in the ferrates, but it has not been isolated.

Ferrous Oxide, Fe_2O_2 or FeO.—This oxide is isomorphous with magnesia, zinc oxide, etc. It is almost unknown in the separate state, from the extreme proneness to absorb oxygen and pass into the sesquioxide. When a ferrous salt is mixed with caustic alkali or ammonia, a bulky whitish precipitate of ferrous hydroxide falls, which becomes anhydrous and nearly black when boiled. This hydroxide changes very rapidly when exposed to the air, becoming green and ultimately red-brown. The soluble ferrous salts have commonly a delicate pale-green colour and a nauseous metallic taste.

Sesquioxide, or *Ferric Oxide*, Fe_2O_3.—Ferric oxide is isomorphous with alumina. It occurs native, most beautifully crystallised as specular iron ore, in the island of Elba, and elsewhere; also as red and brown *hæmatite*, the latter being a hydrate. The two chief varieties of brown hæmatite are called respectively goethite, $Fe_2O_3.H_2O$, and limonite, which is more important, $2Fe_2O_3.3H_2O$. Ferric oxide is artificially prepared by precipitating a solution of ferric sulphate or chloride with excess of ammonia, and washing, drying, and igniting the brown hydrate, thus produced : fixed alkali should not be used in this operation, as a portion is retained by the oxide. In fine powder, this oxide has a full red colour, and is used as a pigment, being prepared for that purpose by calcination of ferrous sulphate ; the tint varies somewhat with the temperature to which it has been exposed. It is also much used for polishing glass and metals. The oxide is unaltered in the fire, although easily reduced at a high temperature by carbon or hydrogen. It dissolves in acids, with difficulty after strong ignition, forming a series of reddish salts, which have an acid reaction and an astringent taste. The ordinary form of ferric oxide is not acted upon by the magnet, but a magnetic variety may be obtained by oxidising the black oxide by fusion with nitre at a moderate temperature.

Ferroso-ferric Oxide, $Fe_3O_4 = FeO,Fe_2O_3$, also called *black iron oxide*, or *magnetic oxide*, occurs as a natural product, *loadstone*, one of the most valuable of the iron-ores, and is often found in regular octahedral crystals, which are magnetic. It may be prepared by mixing due proportions of ferrous and ferric salts, precipitating them with excess of alkali, and then boiling the mixed hydroxides ; the latter then unite to a black sandy substance, consisting of minute crystals of the magnetic oxide. This oxide is the chief product of the oxidation of iron at a high temperature in the air and in aqueous vapour.

Ferrates.—When a mixture of one part of pure ferric oxide and four parts of dry nitre is heated to full redness in a covered crucible, and the resulting brown, porous, deliquescent mass is treated when cold with ice-cold water, a deep amethystine-red solution of potassium ferrate is obtained. The same salt may be more easily prepared by passing chlorine gas through a strong solution of potash in which

recently precipitated ferric hydroxide is suspended; it is then deposited as a black powder, which may be drained upon a tile. It consists of K_2FeO_4 or K_2O,FeO_3, and is therefore analogous in composition to the sulphate and chromate of potassium. The solution of this salt gradually decomposes, even in the cold, and rapidly when heated, giving off oxygen and depositing sesquioxide. The solution of potassium ferrate gives no precipitate with salts of calcium, magnesium, or strontium, but when mixed with a barium salt, it yields a deep crimson, insoluble *barium ferrate*, $BaFeO_4$ or BaO,FeO_3, which is permanent. Neither the hydrogen-salt, ferric acid, H_2FeO_4, nor the corresponding anhydrous oxide, FeO_3, is known in the separate state.

Ferrous Sulphate, $FeSO_4,7H_2O$.—This beautiful and important salt, commonly called *green vitriol*, *iron vitriol*, or *copperas*, may be obtained by dissolving iron in dilute sulphuric acid: it is generally prepared, however, and on a very large scale, by contact of air and moisture with common iron pyrites, which readily absorb oxygen. Heaps of this material are exposed to the air until the decomposition is sufficiently advanced: the salt produced is then dissolved out by water, and the solution is left to crystallise. It forms large green crystals, which slowly effloresce and oxidise in the air: it is soluble in about twice its weight of cold water. Crystals containing 4 and also 2 molecules of water have been obtained. Ferrous sulphate forms double salts with the sulphates of potassium and ammonium, containing $FeK_2(SO_4)_2,6H_2O$ and $Fe(NH_4)_2(SO_4)_2,6H_2O$, isomorphous with the corresponding magnesium salts.

Ferric Sulphate, $Fe_2(SO_4)_3$, is prepared by adding to a solution of the ferrous salt exactly one-half as much sulphuric acid as it already contains, raising the liquid to the boiling-point, and then dropping in nitric acid until the solution ceases to blacken by such addition. The red liquid thus obtained furnishes on evaporation to dryness a buff-coloured amorphous mass, which dissolves very slowly when put into water. With the sulphates of potassium and ammonium, this salt yields compounds having the form and constitution of alums; the potassium salt, for example, has the composition $Fe'''K(SO_4)_2,12H_2O$ or $K_2SO_4.Fe_2(SO_4)_3.24H_2O$. The crystals are nearly colourless; they are decomposed by water, and sometimes by long keeping in the dry state. These iron-alums are best prepared by exposing to spontaneous evaporation a solution of ferric sulphate to which potassium or ammonium sulphate has been added.

Ferrous Nitrate, $Fe(NO_3)_2.6H_2O$.—When dilute cold nitric acid is made to act to saturation upon iron monosulphide, and the solution is evaporated in a vacuum, pale-green and very soluble crystals of ferrous nitrate are obtained, which are very subject to alteration. *Ferric nitrate* is readily formed by dissolving iron in

excess of strong nitric acid, slightly diluted, upon iron; a deep-red liquid is obtained, apt to deposit an insoluble basic salt, and is used in dyeing. The salt crystallises in pale-coloured prisms which are said to have the composition $Fe(NO_3)_3 6H_2O$.

Ferrous Carbonate is obtained as a whitish precipitate, probably an oxysalt, on mixing solutions of ferrous salt and alkaline carbonate: it cannot be washed and dried without losing carbonic acid and absorbing oxygen. This compound occurs in nature as *spathose iron ore*, *iron spar*, or *chalybite*, associated with variable quantities of calcium and magnesium carbonates; also in the common *clay iron stone*, and black band ironstone, from which nearly all the British iron is made. It is often found in mineral waters, being soluble in excess of carbonic acid: such waters are known by the rusty matter they deposit on exposure to the air. No ferric carbonate is known.

Ferrous Phosphate occurs native as *vivianite*, $Fe_3(PO_4)_2.8H_2O$, and is obtainable as a slate-blue precipitate on mixing solutions of ferrous sulphate and sodium phosphate.

Ferric Phosphate, $Fe_2(PO_4)_2$ or $FePO_4$, forms the white precipitate procured by mixing a ferric salt with a soluble phosphate.

Iron Sulphides.—Several compounds of iron and sulphur are known: of these the two most important are the following. The *monosulphide*, or *ferrous sulphide*, FeS, is a blackish brittle substance, attracted by the magnet, formed by heating together iron and sulphur. It is dissolved by dilute acids, with evolution of sulphuretted hydrogen gas, and is constantly employed for that purpose in the laboratory, being made by projecting into a red-hot crucible a mixture of $2\frac{1}{2}$ parts of sulphur and 4 parts of iron filings or borings of cast-iron, and excluding the air as much as possible. The same substance is formed when a bar of white-hot iron is brought into contact with sulphur. The *bisulphide*, FeS_2, or iron pyrites, is a natural product, occurring in rocks of all ages, and evidently formed in many cases by the gradual deoxidation of ferrous sulphate by organic matter. It has a brass-yellow colour, is very hard, not attracted by the magnet, and not acted upon by dilute acids. When it is exposed to heat sulphur is expelled, and an intermediate sulphide, Fe_3S_4, analogous to the black oxide, is produced. This latter substance also occurs native, under the name of *magnetic pyrites*. Iron pyrites is the material now chiefly employed for the manufacture of sulphuric acid; for this purpose the mineral is roasted in a current of air, and the sulphurous oxide formed is passed into the lead chambers; the residue consists of ferric oxide, frequently containing a quantity of copper large enough to render the extraction of that metal remunerative.

Compounds of iron with *phosphorus*, *carbon*, and *silicon* exist, but

little is known respecting them in a definite state. The carbonide is contained in cast iron and in steel, to which it communicates ready fusibility; the silicon-compound is also found in cast iron. Phosphorus is a very hurtful substance in bar iron, rendering it brittle or *cold-short.*

Reactions of Iron Salts.—Ferrous salts are thus distinguished.

Caustic alkalis and *ammonia* give nearly white precipitates, insoluble in excess of the reagent, rapidly becoming green, and ultimately brown, by exposure to air. The *carbonates* of *potassium*, *sodium*, and *ammonium* throw down whitish ferrous carbonate, also very subject to change. *Hydrogen sulphide* gives no precipitate, but *ammonium sulphide* throws down black ferrous sulphide, soluble in dilute acids. *Potassium ferrocyanide* gives a nearly white precipitate, becoming deep-blue on exposure to air: the *ferricyanide* gives at once a deep-blue precipitate.

Ferric salts are thus characterised:

Caustic fixed alkalis and *ammonia* give foxy-red precipitates of ferric hydrate, insoluble in excess. The *carbonates* behave in a similar manner, carbon dioxide escaping. *Hydrogen sulphide* gives a nearly white precipitate of sulphur, and reduces the ferric to ferrous salt. *Ammonium sulphide* gives a black precipitate of ferrous sulphide mixed with sulphur. *Potassium ferrocyanide* yields Prussian blue. Potassium thiocyanate gives an intense orange-red solution, the production of which is perhaps the most delicate test for iron in the ferric state. Tincture or infusion of *gall nuts* or solution of tannin strikes a deep bluish-black with dilute solutions of ferric salts.

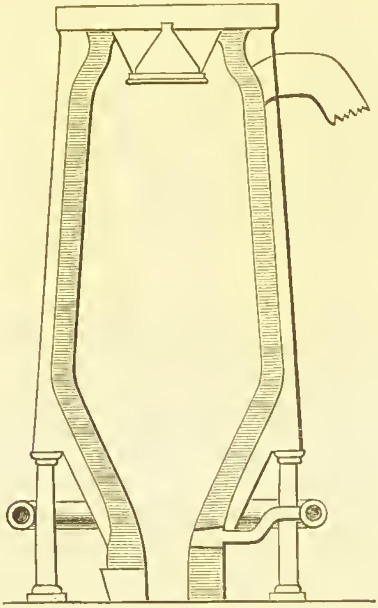
Iron Manufacture.—This important industry may be regarded as yielding three distinct products—namely, cast iron, wrought or malleable iron, and steel—each of which presents characters quite distinct from those of the other two.

The minerals which are available as ores for the extraction of metallic iron consist either of oxide or carbonate, and of each there are several varieties. The more important of these have already been described in the preceding pages, and it will now be sufficient to say that in this country by far the larger proportion of iron is made from the carbonate in the form of *clay-iron stone* obtained from the coal measures, and, in the Cleveland district, from the lias formation.

Clay-iron ore (in Staffordshire, South Wales, and in Scotland) is found in association with coal, forming thin beds or nodules: it consists, as already mentioned, of ferrous carbonate mixed with clay: sometimes lime and magnesia are also present. It is broken in pieces, and exposed to heat in a furnace resembling a lime-kiln, by which the water and carbon dioxide are expelled, and the ore is rendered dark-coloured, denser, and magnetic: it is then ready for reduction. The furnace in which this operation is performed is

usually of very large dimensions, 50 feet or more in height, and constructed of very solid brickwork, inclosed in an outer jacket of iron plates, the interior being lined with excellent fire-bricks. A general idea of the shape may be gained from the section shown in fig. 138, which represents a modern Cleveland furnace 85 feet high, having at the top the cup and cone arrangement, by which the materials are introduced, and a wide pipe by which the gases produced within the furnace can be conveyed away, and turned to account either for heating steam-boilers or for heating the air-blast as explained further on. The furnace is closed at the bottom, the fire being maintained by a powerful artificial blast introduced by *tuyere-pipes.* The materials, consisting of due proportions of coke or coal, roasted ore, and limestone, are constantly supplied from the top, the operation proceeding continuously night and day, often for years, or until the furnace is judged to require repair. In the upper part or shaft of the furnace, where the temperature is still very high, and where combustible gases abound, the iron of the ore is probably reduced to the metallic state, being disseminated through the earthy matter of the ore. As the whole sinks down, the iron and slag, both in the melted state, reach at last the bottom or hearth of the furnace, where they arrange themselves in the order of their densities, the slag floating upon the iron. The slag flows out at certain apertures contrived for the purpose, and the iron is discharged from time to time, and suffered to run into rude moulds of sand by opening an orifice at the bottom of the furnace previously stopped with clay.

Fig. 138.



The general nature of the chemical changes which go on in the blast-furnace are not difficult to explain, though there is much difference of opinion as to some details. The air blown in at the bottom may be supposed to yield oxygen to the carbon of the fuel, producing carbonic oxide directly or carbonic anhydride, which is immediately afterwards reduced to carbonic oxide. It is this gas, carbonic oxide, which plays the most important part in the reduction of the ore. The latter may be supposed to consist essentially of ferric oxide, and the change may be represented by this equation :—

$$3CO + Fe_2O_3 = 3CO_2 + Fe_2.$$

In the presence of more carbon the carbon dioxide is itself reduced again, and these reactions go on alternately as the gas ascends through the furnace until, arriving at the upper part where the temperature is not sufficiently high, the oxide of iron is unaffected. The carbonic oxide then passes off accompanied by the nitrogen of the air, together with a small quantity of hydrocarbons produced when raw coal has been used. The gas which thus escapes is combustible, and it was formerly the custom to allow it to burn at the throat of the furnace, but as already mentioned, it is now carried off and burnt where the heat thus generated can be utilised.

Now metallic iron in the pure state, as liberated from the ore, is not fusible at the temperature existing in the blast furnace, but carbon monoxide at that temperature is decomposed into carbon dioxide and carbon :

$$CO + CO = CO_2 + C.$$

The latter is deposited in the solid form, and slowly combines with the iron, forming a fusible carbide or mixture of carbides, which is the main constituent of cast iron. A little silicon, sulphur, and phosphorus are at the same time reduced from the ore or from the ashes of the coal, and these also combine with the iron. At the same time the lime flux added combines with silica and alumina in the ore and produces the slag, which, with the iron, settles down to the crucible or hearth, and both are drawn off as already explained.

A great improvement in the original mode of conducting the process was the substitution of coke for raw coal, and the blowing of hot air instead of cold into the furnace. This is effected by causing the air, on leaving the blowing-machine, to circulate through a system of iron pipes, or brickwork heated to redness, until its temperature becomes high enough to melt lead. This alteration effects a prodigious saving of fuel, without injury to the quality of the product.

The product of the blast-furnace, commonly known as *cast* or *pig* iron, is a hard and brittle substance which varies considerably in appearance, in composition, and in mechanical properties, according to the nature of the material operated upon, the proportions used, the temperature of the furnace, and other circumstances. It may be regarded as a mixture of compounds of the metal with the elements carbon and silicon, accompanied by small quantities of impurities, chiefly sulphur and phosphorus. While hot, the fluid metal seems to have the power of combining with or dissolving considerable quantities of carbon, but on cooling slowly a certain proportion of this carbon usually separates out in the form of crystalline graphites so that the broken surface presents a dark-grey colour due to the intermixture of black graphitic scales with the metallic carbide. Iron of this character is preferred for use in the foundry for making castings, whilst white cast iron in which the whole, or nearly the whole, of the carbon remains in combination is converted into

wrought iron. The following examples will convey a general idea of the composition of pig iron, though it must be understood that it varies very greatly, and that even the product of the same furnace is not always perfectly uniform in character.

	S. Staffs. Foundry Pig.	Mottled Cleveland Iron.	White Forge Pig from Magnetite.	Red Hæmatite.
Carbon, graphitic, .	3·30	2·70	0·00	3·04
,, combined, .	0·40	0·85	2·50	0·70
Silicon, . . .	1·88	0·66	0·16	2·00
Sulphur, . .	0·02	0·35	0·04	0·01
Phosphorus, . .	0·71	1·05	0·11	0·03
Manganese, . .	0·40	0·79	0·10	0·31
Iron, . . .	93·29	93·59	97·09	93·91
	100·00	99·99	100·90	100·00

The composition of blast-furnace slag varies a good deal, though perhaps less than might be expected from the considerable differences in appearance exhibited by samples from different furnaces, or even from the same furnace if the conditions are varied. Slag is a stony or semi-vitreous-looking substance, showing various shades of blue, or greenish-grey, or brown, or even black when much iron is present. The following figures give the mean of thirteen analyses by Mr E. Riley, and sufficiently indicate the general nature of this material :—

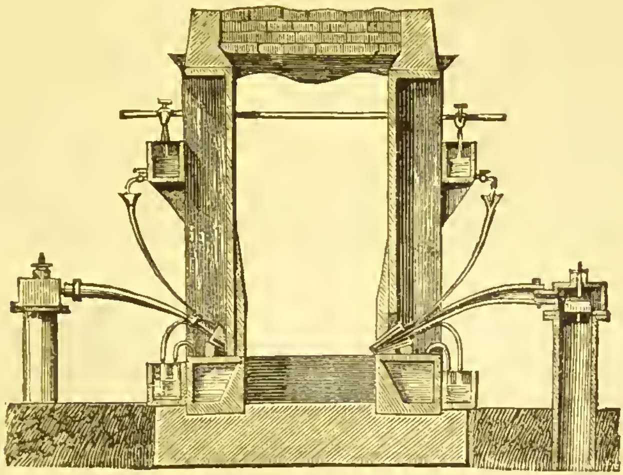
Silica, SiO_2, ...	41·85	87·57
Alumina, Al_2O_3, ...	14·73	
Lime, CaO, ...	30·99	
Ferrous oxide, FeO, ...	2·63	12·75
Manganous oxide, MnO, . . .	1·24	
Magnesia, MgO, ...	4·76	
Potash, K_2O, ...	1·90	
Calcium, ...	1·15	
Sulphur, ...	0·92	
Phosphoric oxide, P_2O_5, . . .	0·15	
	100·32	

Slag is used to a small extent as road-metal, for brick and cement making, and is also blown into a finely-fibrous material called slag-wool, which is employed as covering for steam pipes. The heat of the slag as it flows from the furnace is also sometimes utilised for evaporating brine in salt-making.

The conversion of cast into wrought iron is effected chiefly by an operation called *puddling*, the object of which is to remove as far as

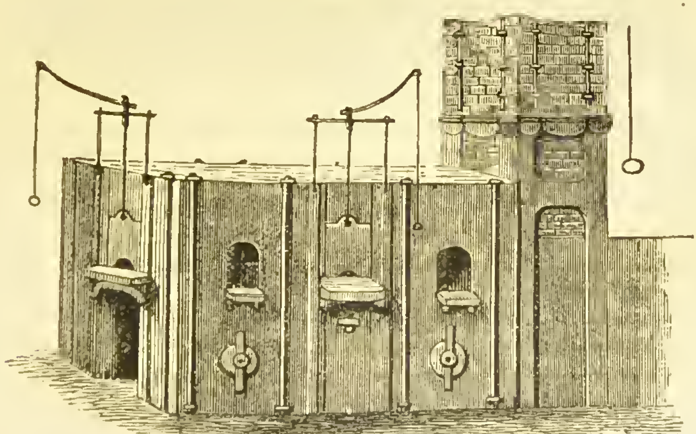
possible the carbon and silicon, and other substances present in cast iron. The process of puddling is sometimes preceded by an operation called *refining*, which consists in remelting it, in contact with the fuel, in small low furnaces called *refineries*, while air is blown

Fig. 139.



over its surface by means of tuyeres. Figure 139 represents a vertical section of a refinery. The apparatus consists of a rectangular trough of cast iron, the walls of which are kept cool by

Fig. 140.

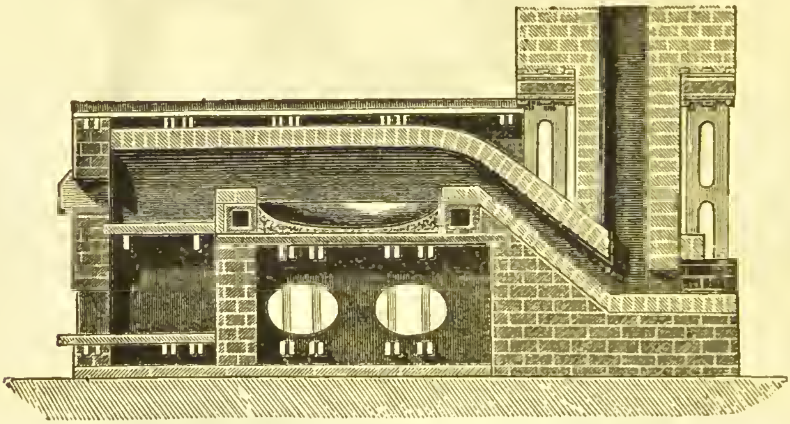


water and lined with fireclay. There are usually six pipes or tuyeres, three on each side, by which the air is blown upon the surface of the molten metal. A fire is first made upon the hearth of

the refinery, and the pigs of cast iron having been laid in order and covered with coke, the blast is turned on till the metal is completely melted. The effect of this operation is to deprive the iron of a great part of the silicon and some of the carbon associated with it. The metal thus purified is run out into a trench, and suddenly cooled, by which it becomes white, crystalline, and exceedingly hard.

The *puddling* process is conducted in a reverberatory furnace (figs. 140 and 141), into which the charge of crude or of fine metal is introduced by a side aperture. The hearth is hollowed out and lined with a "*fettling*" of pure oxide of iron. The metal is speedily melted by the flame, and its surface covered with a siliceous slag. The workman then, by the aid of an iron tool, diligently stirs the melted mass, which at a certain stage appears to boil, so as intimately to mix the oxide with the metal. Small jets of blue flame soon appear upon the surface of the iron, and the latter, after a time, begins to lose its

Fig. 141.



fluidity, and acquires, in succession, a pasty and a granular condition. At this point the fire is strongly urged, the sandy particles once more cohere, and the contents of the furnace now admit of being formed into several large balls or *blooms*, which are then withdrawn, and placed under an immense hammer, moved by machinery, by which each ball becomes quickly fashioned into a rude bar. This is reheated, and passed between grooved cast iron rollers, and drawn out into a long bar or rod. To make the best iron, the bar is cut into a number of pieces, which are afterwards piled or bound together, again raised to a welding heat, and hammered or rolled into a single bar; and this process of *piling* or *fagotting* is sometimes twice or thrice repeated, the iron becoming greatly improved thereby.

The general nature of the change in the puddling furnace is as follows. Cast iron consists essentially of iron in combination with carbon and silicon and these compounds, when strongly heated with iron oxide, undergo decomposition, the carbon and silicon

becoming oxidised at the expense of the oxygen of the oxide. As this change takes place, the metal gradually loses its fusibility, but retains a certain degree of adhesiveness, so that when at last it comes under the tilt-hammer, or between the rollers, the particles of iron become agglutinated into a solid mass, while the readily fusible silicate of the oxide is squeezed out and separated.

The following analyses of pig iron and of the same after refining, and after puddling and rolling, show the extent of the change in composition which the metal suffers in passing through these processes :—

	Cold Blast Pig.	Refined Metal.	Finished Wrought Iron.
Carbon, . .	3·656	3·342	0·226
Silicon, . .	1·255	0·130	0·109
Sulphur, . .	0·033	0·025	0·012
Phosphorus, . .	0·565	0·490	0·064

Wrought iron represents the nearest approach to the pure metal which can be produced by manufacturing processes upon a large scale. Its mechanical properties are totally distinct from those of cast iron ; for while the latter is hard, crystalline, and brittle, the former is soft, fibrous in texture, and readily malleable and ductile. Its capability of *welding* at a red heat, already referred to, also distinguishes it not only from cast iron, but from all but the softest kinds of steel.

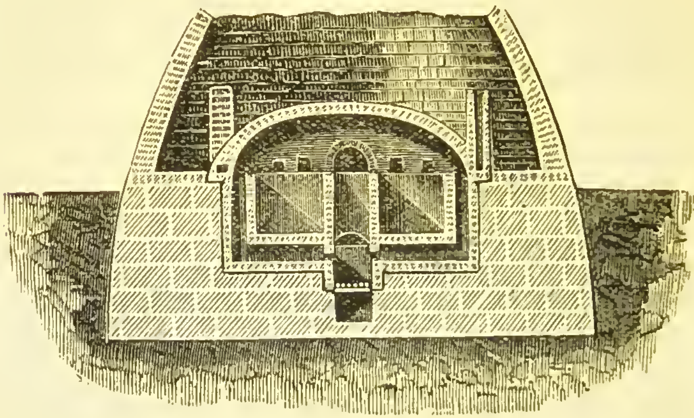
All these processes are, in Great Britain, performed with coal or coke ; but the iron obtained is, in some respects, inferior to that made in Sweden and Russia from the magnetic oxide, by the use of wood charcoal—a fuel too dear to be extensively employed in England. Plate iron is, however, sometimes made with charcoal.

Steel may be obtained by a great variety of processes, all of which have for their object the production of a pure carbide of iron, containing a small regulated quantity of carbon with only minute quantities of silicon, sulphur, and phosphorus. One of the oldest of these is the process called *cementation*, in which bars of, preferably, Swedish iron are imbedded in charcoal powder, contained in a large rectangular chest of fire-brick, and exposed for several days to a full red heat. The accompanying figure shows a section of the lower part of such a converting furnace, the upper part consisting of a conical brick dome which serves to promote regularity of temperature within. The iron takes up, under these circumstances, from $\frac{1}{2}$ to $\frac{3}{4}$, or more, per cent. of carbon, becoming harder, and at the same time more fusible, but with a certain diminution of malleability. The active agent in this cementation process is probably carbon monoxide ; the oxygen of the air in the crucible unites with the carbon to form that compound, which is afterwards decomposed by the heated iron, one-half of its carbon being abstracted by the latter. The carbon dioxide thus formed takes up an additional dose of carbon from the charcoal, and again becomes monoxide, the oxygen, or rather the

carbon dioxide, acting as a carrier between the charcoal and the metal. The product of this operation is called *blistered* steel, from the blisters which appear on the surface of the bars: the texture is afterwards improved and equalised by welding a number of these bars together, and drawing the whole out under a light-tilt hammer, or the bars may be broken up and melted in crucibles.

The operation, which is known as *case-hardening*, is in reality a rapid process of cementation. It is usually applied to small articles, such as keys, which may be shaped from wrought iron, and subsequently hardened superficially by sprinkling them, while red hot,

Fig. 142.



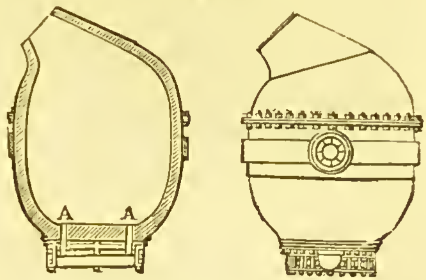
with ferrocyanide of potassium or horn-shavings, and then plunging into water.

The most perfect kind of steel is that which has undergone fusion having been cast into ingot-moulds, and afterwards hammered: of this all fine cutting instruments are made. It is difficult to forge, requiring great skill and care on the part of the operator.

Steel may also be made directly from some particular varieties of cast iron, as that from spathose iron ore containing a little manganese. The metal is retained, in a melted state, on the hearth of a furnace, while a stream of air plays upon it, and causes partial oxidation: the oxide produced reacts, as before stated, on the carbon of the iron, and withdraws a portion of that element. When a proper degree of stiffness or pastiness is observed in the residual metal, it is withdrawn and hammered or rolled into bars. The *wootz*, or native steel of India, is probably made in this manner. Annealed or malleable cast iron is much employed as a substitute for the more costly products of the forge: the articles when cast are imbedded in powdered hæmatite, and, after being exposed to a moderate red heat for some time, are allowed to cool slowly, by which a very great degree of softness and malleability is attained. Some superficial decarbonisation takes place during this process.

Bessemer steel is a remarkable product, manufactured on an enormous scale by blowing atmospheric air through melted cast iron till the carbon and silicon are removed, and subsequently introducing the requisite amount of carbon, together with some manganese.

Fig. 143.



The operation is conducted in an iron vessel called the *converter*, of the form represented in the figure, and lined with infusible material. Considerable heat is generated by the oxidation of the carbon and silicon, so that the temperature is kept above the melting-point of steel during the whole of the operation. When the decarburation has been carried far enough, the current of air is stopped, and a small quantity of speigel-eisen or ferromanganese is dropped into the liquid metal, which, after a few minutes' rest, is poured into ingot-moulds.

In the original Bessemer process the converter was lined with a siliceous kind of fireclay called *ganister*, and it was found that, although the carbon and silicon, beside a portion of the iron, were readily oxidised, the phosphorus and sulphur usually present were not removed. As the presence of these elements in more than the most minute quantity is very detrimental to the quality of the resulting steel, it was necessary to select for this process pig iron containing the minimum amount of sulphur and phosphorus, with a relatively large proportion of silicon. By employing a mixture of lime and magnesia (calcined dolomite) for lining the converter, Thomas and Gilchrist succeeded in making good steel from pig iron containing large quantities of phosphorus. This modification constitutes the *basic* Bessemer process, by which large quantities of steel are now manufactured.

Another method of steel-making is that known as the Siemens-Martin process, which consists in dissolving scrap iron in molten pig iron heated in a reverberatory furnace, or in adding pure oxides of iron to cast iron previously melted. In both cases a certain proportion of speigel-eisen is added at the end of the process.

The most remarkable property of steel is that of becoming exceedingly hard when quickly cooled. When heated to redness, and suddenly quenched in cold water, steel, in fact, becomes capable of scratching glass with facility; if reheated to redness, and once more left to cool slowly, it again becomes nearly as soft as ordinary iron; and between these two conditions, any required degree of hardness may be attained. The articles, forged into shape, are first hardened in the manner described; they are then *tempered* or *let down*, by exposure to a proper degree of annealing heat, which is often judged of by the colour of the thin film of oxide which appears on the

polished surface. Thus, a temperature of about 221° C. (430° F.), indicated by a faint straw colour, gives the proper temper for razors; that for scissors, penknives, etc., is comprised between 243° and 254° C. (470–490° F.), and is indicated by a full yellow or brown tint. Swords and watch-springs require to be softer and more elastic, and must be heated to 288° or 293° C. (500–560° F.), or until the surface becomes deep-blue. Attention to these colours has now become of less importance, as metal baths are often substituted for the open fire in this operation.

COBALT.

Symbol, Co. Atomic weight, 59.

This metal occurs in combination with sulphur in linnæite, Co_3S_4; with arsenic in skutterudite, $CoAs_3$; with sulphur and arsenic in speiss-cobalt, $(Co,Ni,Fe)As_2$, and cobalt-glance, $(Co,Fe)(AsS)_2$; as arsenate in erythrin or cobalt-bloom, $Co_3(AsO_4)_2, 8H_2O$; and associated with manganese in wad, $(Co,Mn)O,2MnO_2,4H_2O$. It is an almost invariable constituent of meteoric iron, and has been detected spectroscopically in the atmosphere of the sun.

Cobalt-compounds may be prepared from speiss or any arsenical cobalt-ore by the following process:—The mineral is broken into small fragments, mixed with from one-fourth to half its weight of iron filings, and the whole is dissolved in nitro-muriatic acid. The solution is gently evaporated to dryness, the residue treated with boiling water, and the insoluble iron arsenate removed by a filter. The liquid is then acidulated with hydrochloric acid, treated with hydrogen sulphide in excess, which precipitates the copper, and after filtration, boiled with a little nitric acid to bring back the iron to the ferric state. To the cold and largely diluted liquid solution, sodium bicarbonate is gradually added, by which the ferric oxide may be completely separated without loss of nickel-salt. Lastly, the filtered solution, boiled with sodium carbonate in excess, yields an abundant precipitate of cobalt carbonate, more or less mixed with nickel carbonate.

The separation of cobalt from nickel may be effected by the following process, devised by H. Rose. A solution of the chlorides is supersaturated with chlorine gas, and then mixed with excess of recently precipitated barium carbonate, left at rest for twelve to eighteen hours, and shaken up from time to time. The whole of the cobalt is thereby thrown down as sesquioxide, while the nickel remains in solution. A method commonly used which is based upon practically the same principle consists in adding to the solution of the mixed chlorides a solution of bleaching powder in successive moderate quantities. The cobalt is first precipitated in the form of the black sesquioxide, while the nickel remains in solution. A solution of cobalt free from nickel may also be obtained by preci-

pitating the mixed solution with oxalic acid : the whole of the nickel is thereby precipitated, together with a small portion of the cobalt leaving pure cobalt in solution. Other methods will be described in connection with nickel.

Cobalt is a white, malleable, and tenacious metal, having a density 8·5, and a very high melting-point. It is unchanged in the air, and but feebly attacked by dilute hydrochloric and sulphuric acids. It is strongly magnetic.

Cobalt forms two classes of salts, analogous in composition to the ferrous and ferric salts; but the cobaltic salts, in which the metal is apparently trivalent, are, with the exception of the nitrite, very unstable.

Chlorides.—*Cobaltous Chloride*, $CoCl_2$, is easily prepared by dissolving the oxide in hydrochloric acid; or it may be prepared directly from *cobalt-glance*, the native arsenide, by the process above described. It forms a deep rose-red solution, which, when sufficiently strong, deposits hydrated crystals of the same colour; when the liquid is evaporated by heat to a very small bulk, it deposits anhydrous crystals, which are blue : these latter by contact with water again dissolve to a red liquid. A dilute solution of cobalt chloride constitutes the well-known *blue sympathetic ink:* characters written on paper with this liquid are invisible, from their paleness of colour, until the salt has been rendered anhydrous by exposure to heat, when the letters appear blue. On laying it aside, moisture is absorbed, and the writing once more disappears. Green sympathetic ink is a mixture of the chlorides of cobalt and nickel.

Cobaltic Chloride, Co_2Cl_6, is obtained in solution by dissolving the sesquioxide in hydrochloric acid, and in small quantity by saturating a solution of the dichloride with chlorine gas. The liquid has a dark-brown colour, but easily decomposes, giving off chlorine and leaving the rose-coloured dichloride.

Bromide and *Iodide* of cobalt are similar in character to the chloride. The cobaltous iodide affords a remarkable instance of changes of colour during hydration, the anhydrous compound, CoI_2, being black and lustrous like graphite, but on exposure to moist air it assumes a moss-green colour, forming the hydrate $CoI_2 2H_2O$. By solution in water a pink compound is produced, which may be obtained in crystals of the formula $CoI_2.6H_2O$.

Oxides and Oxysalts.—Cobalt forms a monoxide and a sesquioxide, also two or three oxides of intermediate composition. The *monoxide*, or *cobaltous oxide*, CoO, is a grey powder soluble in acids, and is isomorphous with magnesia, affording salts of a fine red tint. It is prepared by precipitating cobaltous sulphate or chloride with sodium carbonate, and washing, drying, and igniting the precipitate. When the cobalt solution is mixed with caustic potash, a beautiful blue precipitate falls, which, when heated, becomes violet, and at length dirty red, from absorption of oxygen and a change in the state of hydration.

The *Sesquioxide*, or *Cobaltic Oxide*, Co_2O_3, is a black, insoluble, neutral powder, obtained by mixing solutions of cobalt and chloride of lime. It dissolves in acids, yielding the cobaltic salts.

Cobaltoso-cobaltic Oxide, Co_3O_4, a black crystalline powder, analogous to the magnetic oxide of iron, is formed when cobaltous nitrate or oxalate, or hydrated cobaltic oxide, is heated in contact with the air.

Cobaltic Acid, H_2CoO_4, the analogue of ferric and chromic acids appears to be formed when to a solution of any salt of cobalt excess of sodium bicarbonate is added, followed by hydrogen peroxide. A green solution is formed, and though the salt has not been isolated, experiment shows that the maximum green colour is produced when the molecular proportions of cobalt salt and hydrogen peroxide are 1 to 2;

$$CoCO_3 + 2H_2O_2 = H_2CoO_4 + CO_2 + H_2O.$$

The green solution may be formed in presence of nickel salts, and the reaction serves for the detection of cobalt in the presence of nickel, even in large excess. (Durrant.)

Oxide of cobalt is remarkable for the magnificent blue colour it communicates to glass: indeed, this is a character by which its presence may be most easily detected, a very small portion of the substance to be examined being fused with borax on a loop of platinum wire before the blow-pipe; the production of this colour both in the inner and in the outer flame distinguishes cobalt from all other metals.

The substance called *smalt*, used as a pigment, consists of glass coloured by cobalt: it is thus made:—The cobalt ore is roasted until nearly free from arsenic, and then fused with a mixture of potassium carbonate and quartz-sand, free from oxide of iron. Any nickel that may happen to be contained in the ore then subsides to the bottom of the crucible as arsenide: this is the *speiss* already mentioned. The glass, when complete is removed and poured into cold water; it is afterwards ground to powder and elutriated. *Cobalt ultramarine* is a fine blue colour prepared by mixing 16 parts of freshly precipitated alumina with 2 parts of cobalt phosphate or arsenate: this mixture is dried and slowly heated to redness. By daylight the colour is pure blue, but by artificial light it is violet. A similar compound, of a fine green colour, is formed by igniting zinc oxide with cobalt-salts. *Zaffre* is the roasted cobalt ore mixed with siliceous sand, and reduced to fine powder: it is used in enamel painting. A mixture in due proportions of the oxides of cobalt, manganese, and iron is used for giving a fine black colour to glass.

Cobaltous Salts.—The *Sulphate*, $CoSO_4,7H_2O$, forms red crystals, requiring for solution 24 parts of cold water; they are identical in form with those of magnesium sulphate. It combines with the sulphates of potassium and ammonium, forming double salts containing 6 molecules of water.

A solution of oxalic acid added to cobaltous sulphate occasions

after some time, the separation of nearly the whole of the base in the state of oxalate.

The *carbonate* is thrown down by the alkaline carbonates from solutions of cobalt, as a pale peach-blossom-coloured precipitate of combined carbonate and hydroxide, containing $2CoCO_3,3CoH_2O_2+H_2O$.

Cobaltic Salts.—Cobaltic oxide dissolves in cold acids, forming brown solutions which are easily decomposed, the oxysalts evolving oxygen and the chloride evolving chlorine. The most stable of these salts is the *acetate*, the solution of which gives brown precipitates with alkalis and sodium phosphate, and a black precipitate with ammonium sulphide.

Greater stability is exhibited by certain double cobaltic salts, the most important of which is:

Potassio-cobaltic Nitrite, $K_6Co_2(NO_2)_{12},nH_2O$, which is obtained as a yellow precipitate on adding potassium nitrite to the solution of a cobaltous salt, the chloride for example, acidulated with acetic acid, the reaction being represented by the equation :—

$$2CoCl_2 + 10KNO_2 + 4HNO_2 = K_6Co_2(NO_2)_{12} + 4KCl + 2NO + 2H_2O.$$

This compound, called *cobalt-yellow*, is a bright yellow powder composed of microscopic pyramids or stellate forms. It is usually anhydrous, but may be obtained, according to the strength of the solution with 1 to 4 molecules of water, its colour then varying from bright yellow to a dark greenish-yellow. It is decomposed by nitric and hydrochloric acids, with aid of heat, slowly by caustic potash, but quickly by caustic soda or baryta at a gentle heat, yielding a precipitate of brown cobaltic hydroxide. When suspended in water, it is slowly attacked by hydrogen sulphide, quickly by ammonium sulphide, with formation of black cobalt sulphide. Corresponding double salts are also known, containing sodium, ammonium, and thallium.

Ammoniacal Cobalt Compounds.—Cobaltous salts, treated with ammonia in a vessel protected from the air, unite with the ammonia, forming compounds which may be called ammonio-cobaltous salts. Most of them contain 6 molecules of ammonia to 1 molecule of the cobalt salt; thus the chloride contains $CoCl_2,6NH_3+H_2O$; the nitrate, $Co(NO_3)_2 6NH_3+2H_2O$. They are generally crystallisable, and of a rose colour, soluble without decomposition in ammonia, but decomposed by water, with formation of a basic salt. H. Rose, by treating dry cobalt chloride with ammonia gas, obtained the compound $CoCl_2,4NH_3$; and in like manner an ammonio-sulphate has been formed containing $CoSO_4,6NH_3$.

When an ammoniacal solution of cobalt is exposed to the air, oxygen is absorbed, the liquid turns brown, and new salts are formed. Most of the peroxidised ammonio-cobalt salts are com-

posed of cobaltic salts united with two or more molecules of ammonia. The composition of the normal salts may be illustrated by the chlorides, as in the following table :—

Tetrammonio-cobaltic chloride, . .	$Co_2Cl_6(NH_3)_4$
Hexammonio-cobaltic chloride, . .	$Co_2Cl_6(NH_3)_6$
Octammonio cobaltic (or praseo-cobaltic) chloride, ...	$Co_2Cl_6(NH_3)_8$
Decammonio-cobaltic (roseo- and purpureo-cobaltic) chloride, . . .	$Co_2Cl_6(NH_3)_{10}$
Dodecammonio-cobaltic (or luteo-cobaltic) chloride, ...	$Co_2Cl_6(NH_3)_{12}$

The formulæ of the corresponding normal nitrates are deduced from the preceding by substituting NO_3 for Cl ; those of the sulphates, oxalates, and other bibasic salts, by substituting SO_4, C_2O_4, etc., for Cl_2, *e.g.*, *decammonio-cobaltic sulphate* $= Co_2(SO_4)_3(NH_3)_{10}$. There are also acid and basic salts of the same ammonium-molecules, such as the *oxyoctammonio-cobaltic* or *fusco-cobaltic salts*, which may be regarded as basic praseo-cobaltic salts, *e.g.*, the *hydroxynitrate*, $Co_2(NO_3)_4(OH)_2(NH_3)_8$. Further, there are salts containing the radicles NO and NO_2, in addition to ammonia, *e.g.*, *decammonio-nitroso-cobaltic* or *xantho-cobaltic chloride*, $Co_2Cl_4(NO_2)_2(NH_3)_{10}$, which may be regarded as roseo- or purpureo-cobaltic salts, in which one-third of the chlorine or other acid radicle is replaced by NO_2. Lastly, ammoniacal compounds (*oxycobaltic salts*) containing salts of cobalt corresponding with the dioxide have been obtained by Frémy and several other chemists.

C o b a l t o u s s a l t s have the following characters :—

Solution of *potash* gives a blue precipitate, changing by heat to violet and red. *Ammonia* gives a blue precipitate, soluble with difficulty in excess with brownish-red colour. *Sodium carbonate* forms a pink precipitate. *Ammonium carbonate*, a similar compound, soluble in excess. *Potassium ferrocyanide* gives a greyish-green precipitate. *Potassium cyanide* forms a yellowish-brown precipitate, which dissolves in an excess of the precipitant. The clear solution, after boiling, may be mixed with hydrochloric acid without giving a precipitate. *Hydrogen sulphide* produces no change, if the cobalt is combined with a strong acid. *Ammonium sulphide* throws down black sulphide of cobalt, insoluble in dilute hydrochloric acid.

C o b a l t i c s a l t s, formed by dissolving cobaltic oxide in acids, give with *potash*, a dark-brown precipitate of hydrated cobaltic oxide ; with ammonia, a brownish-red solution ; with the *fixed alkaline carbonates*, a green solution, which deposits a small quantity of cobaltic oxide ; with *ammonium sulphide* (after saturation of the free acid by ammonia), a black precipitate.

For the detection of minute quantities of cobalt, the deep blue coloration obtained on mixing together solutions of cobaltous salts with potassium thiocyanate, or the green coloration developed by

the addition of sodium bicarbonate and hydrogen peroxide may be turned to account.

Probably the most delicate and characteristic test is the production of a blue glass when borax is fused on a platinum loop with any cobalt compound, in either the oxidising or reducing flame.

NICKEL.

Symbol, Ni. Atomic weight, 58.

This metal, as already observed, is a constant constituent of meteoric iron. It is found in tolerable abundance in some of the metal-bearing veins of the Saxon mountains of Westphalia, in Hesse, Hungary, and Sweden, chiefly as arsenide, Ni_2As_2, the *kupfernickel* of mineralogists, so called from its yellowish-red colour. The word *nickel* is a term of detraction, having been applied by the old German miners to what was looked upon as a kind of false copper ore. The artificial, or perhaps merely fused product, called *speiss*, has nearly the same composition. A valuable source of nickel has been found in Garnierite, a silicate of nickel and magnesium largely imported of late years from New Caledonia.

From either of these substances a pure salt of nickel may be obtained in the manner already described in connection with cobalt-salts (p. 486).

Nickel is manufactured from the silicate which contains practically no cobalt, by first converting the metal into a sulphide and then subjecting it to a series of alternate roastings and fusions, whereby the iron present in the ore is eliminated, and the nickel ultimately obtained in the form of pure oxide. This compound is then reduced by mixing it with flour, and making the mixture into cakes, which are heated strongly in crucibles. Discs or blocks of metal are thus obtained, which, when pure, can only be melted at the highest temperature of a wind-furnace.

The arsenides and sulphides of nickel contain so many other metals, including cobalt, that a much more complicated process is necessary for the extraction of the nickel. In outline it is somewhat as follows :—The ores are first roasted with the object of expelling arsenic and sulphur, and obtaining oxides of the metals. These are then dissolved out from the siliceous matters by means of hydrochloric acid, and the acid solution, partially neutralised by lime, is mixed cautiously with bleaching powder, which throws down the iron partly in the form of peroxide, partly as arsenate. The filtered liquor is then treated with sulphuretted hydrogen gas, whereby copper with lead, antimony, and bismuth, when present, are precipitated as sulphides. The liquid is again filtered, and the cobalt precipitated as peroxide by the addition of bleaching powder. Finally, the filtrate is boiled with lime, and the oxide of nickel precipitated

A new process, based upon the formation and decomposition of the remarkable volatile nickel-carbonyl, $Ni(CO)_4$, has been introduced by Mr Mond. The oxides, containing several other metals, such as copper, iron, and cobalt, as well as nickel, are heated gently in a stream of carbonic oxide gas, whereby they are reduced to the metallic state. The nickel, as soon as it is liberated, combines with carbon monoxide and passes off with the excess of that gas into a tube heated by a furnace, and here the nickel-carbonyl is resolved into metallic nickel, which is deposited as a shining compact metallic crust upon the walls of the tube, while carbonic oxide passes on to be circulated through the apparatus and made to do duty again. The other metals do not combine in the same way with carbonic oxide to form volatile compounds, and hence are left behind when the nickel is carried off.

Metallic nickel is easily prepared on a small scale by exposing the oxalate to a white heat, in a crucible lined with charcoal, or by reducing one of the oxides by means of hydrogen at a high temperature. It is a white, malleable metal, having a density 8·8, a high melting-point, and a smaller degree of oxidability than iron, since it is but little attacked by dilute acids. Nickel is strongly magnetic, but loses this property when heated to 350°.

Nickel is used for the preparation of a white alloy, sometimes called German silver, made by melting together 100 parts of copper, 16 of zinc, and 40 of nickel. This alloy is very malleable, and takes a high polish.

Alloys of copper with nickel and zinc, or with nickel alone, are also used in Germany, Belgium, Switzerland, and the United States, for the manufacture of small coin. The advantages of nickel coining are that, nickel being dearer than copper, the coins can be made smaller for the same value; that the alloy is hard and therefore wears well; and further, that its manufacture requires experienced workmen and the use of powerful machinery.

Another application is the electrolytic deposition of nickel on iron, steel, copper, brass, and other metals, from a solution of nickel sulphate or the double sulphate or chloride of nickel and ammonium, or nickel and potassium. The nickel is deposited in dense layers, capable of receiving a good polish.

Nickel forms only one class of salts which correspond to the ferrous and cobaltous compounds. The sesquioxide is not salifiable.

Nickel Carbonyl, $Ni(CO)_4$.—This remarkable compound is obtained by passing carbonic oxide gas over gently heated metallic nickel in the porous state in which it is left by reducing the oxide at not too high a temperature by hydrogen. The product passes off with the excess of carbonic oxide gas, but may be condensed into a colourless liquid, which boils without decomposition at 43°. When the vapour is transmitted through a strongly heated tube it is completely resolved into metallic nickel and carbon monoxide gas. Small quantities of the vapour diffused through that gas confer upon

it the power of giving, when burnt, a highly luminous flame, from which metallic nickel is deposited in the form of a shining black mirror upon a cold porcelain surface held in it. No compound of corresponding composition has been obtained with cobalt or any other metal, with the single exception of iron, which yields, though less easily, a volatile liquid having the formula $Fe(CO)_5$.

Nickel Chloride, $NiCl_2$, is easily prepared by dissolving oxide or carbonate of nickel in hydrochloric acid. A green solution is obtained, which furnishes crystals of the same colour containing water. When rendered anhydrous by heat, the chloride is yellow, unless it contains cobalt, in which case it has a tint of green.

Nickel Oxides and Oxysalts.—Nickel forms two oxides analogous to the two principal oxides of iron.

The *Monoxide*, NiO, is prepared by heating the nitrate to redness, or by precipitating a soluble nickel salt with caustic potash, and washing, drying, and igniting the apple-green hydroxide thrown down. It is an ashy-grey powder, freely soluble in acids, which it completely neutralises, forming salts isomorphous with those of magnesium and the other members of the same group. Nickel salts, when hydrated, have usually a beautiful emerald-green colour; in the anhydrous state they are yellow.

The *Sesquioxide*, Ni_2O_3, is a black insoluble substance, prepared by passing chlorine through the hydroxide suspended in water; nickel chloride is then formed, and the oxygen of the oxide decomposed is transferred to a second portion. It is also produced when a salt of nickel is mixed with a solution of bleaching powder. The sesquioxide is decomposed by heat, and evolves chlorine when treated with hydrochloric acid.

Nickel Sulphate, $NiSO_4,7H_2O$.—This is the most important of the nickel salts. It forms green prismatic crystals, which require 3 parts of cold water for solution. Crystals with 6 molecules of water have also been obtained. It forms with the sulphates of potassium and ammonium beautiful double salts, $NiK_2(SO_4)_2,6H_2O$, and $Ni(NH_4)_2(SO_4)_2,6H_2O$, isomorphous with the corresponding magnesium salts.

When a strong solution of oxalic acid is mixed with sulphate of nickel, a pale bluish-green precipitate of oxalate falls after some time, very little nickel remaining in solution. The oxalate can thus be obtained for preparing the metal.

Nickel Carbonate.—When solutions of nickel sulphate or chloride and of sodium carbonate are mixed, a pale green precipitate falls, which is a combination of nickel carbonate and hydroxide. It is readily decomposed by heat.

Nickel-salts are well characterised by their behaviour with reagents.

Caustic alkalis give a pale apple-green precipitate of hydroxide, insoluble in excess. *Ammonia* affords a similar precipitate, which is soluble in excess, with deep purplish-blue colour. *Potassium* and *sodium carbonates* give pale-green precipitates. *Ammonium carbonate*, a similar precipitate, soluble in excess, with blue colour. *Potasssium ferrocyanide* gives a greenish-white precipitate. *Potassium cyanide* produces a green precipitate, which dissolves in an excess of the precipitant to an amber-coloured liquid, and is reprecipitated by addition of hydrochloric acid. *Hydrogen sulphide* occasions no change, if the nickel be in combination with a strong acid. *Ammonium sulphide* produces a black precipitate of nickel sulphide, which dissolves slightly in excess of the precipitant, with dark-brown colour. Nickel sulphide when once precipitated, is insoluble in dilute hydrochloric acid; it is soluble in nitromuriatic and in hot nitric acid.

METALS OF THE CHROMIUM GROUP.

Chromium.	Tungsten.
Molybdenum.	Uranium.

THIS group of metals is distinguished by the remarkable diversity of their compounds which show singular varieties of colour, the lower grades of oxidation exhibiting blue or greenish colour, while the higher states of oxidation are usually indicated by a yellow or red colour.

The lowest series of chromium compounds correspond in composition with ferrous salts, but no similar compounds are formed by the other members of the group. The most marked general characteristic is the tendency which all display towards the production of acidic trioxides and corresponding salts, in which the acid anhydride frequently occurs in excess; for example there are not only chromates, M_2CrO_4 or $M_2O.CrO_3$ but anhydrochromates, M_2O2CrO_3 and $M_2O.3CrO_3$.

The valency of chromium is well defined, but while molybdenum tungsten and uranium are probably also hexads, they produce anomalous oxides and chlorides, *e.g.*, $MoCl_4$ and $MoCl_5$; WCl_4, WCl_5, and WCl_6; UCl_4 and UCl_5.

CHROMIUM.

Symbol, Cr. Atomic weight, 52.

Chromium is found in the state of sesquioxide, in combination with ferrous oxide, constituting the mineral chrome-ironstone, $FeOCr_2O_3$, corresponding with magnetic iron. Chrome ochre, a yellowish green earthy substance, occurs somewhat abundantly in the Shetland Islands, and elsewhere. Lead chromate, $PbCrO_4$, constitutes a very beautiful mineral, from which the metal was first obtained. The metal itself is obtained in a half-fused condition by mixing the oxide with half its weight of charcoal powder, enclosing the mixture in a crucible lined with charcoal, and then subjecting it to the very highest heat of a powerful furnace.

Chromium has been obtained in small quantities in various other ways, but the most successful method is that of Moissan, who has prepared more than 20 kilograms of the metal by reduction of the oxide in the electric furnace. A cavity is cut in a block of limestone and this is lined with carbon and covered with a lid of the same. Within this cavity an electric arc, produced by a current

of 600 ampères and 60 volts, can be taken between carbon rods, and when a mixture of chromic oxide and carbon in due proportions is exposed to the high temperature thus produced, 2 kilos. of fused metallic chromium can be obtained in about an hour. The product contains carbon, but if this is broken up, placed in a carbon crucible lined with chromic oxide, covered with the same oxide and again subjected to the action of the arc, metallic chromium is obtained quite free from carbon.

Pure chromium is a white metal of specific gravity 6·92 at 20°. It scratches glass but not quartz. On exposure to the air it oxidises superficially only, and afterwards undergoes no further change. When heated strongly in oxygen or in sulphur vapour it burns brilliantly.

The melting point of chromium is considerably higher than that of platinum and cannot be reached by the oxyhydrogen flame. In the electric furnace, however, considerable quantities can be completely melted and as much as 10 kilos. has been melted at once and cast into ingots.

Chromium unites with carbon in several proportions forming extremely hard crystalline compounds. The pure metal is not magnetic.

Aqueous hydrochloric acid and dilute sulphuric acid attack the metal very slowly in the cold though more rapidly on heating, with production of a blue chromous salt.

Chlorides.—*Chromous Chloride*, $CrCl_2$, is prepared by heating the violet-coloured trichloride, contained in a porcelain or glass tube, to redness in a current of perfectly dry and pure hydrogen gas; hydrochloric acid is then disengaged, and a white foliated mass is obtained, which dissolves in water with great elevation of temperature, yielding a blue solution, which on exposure to the air, absorbs oxygen with extraordinary energy, acquiring a deep green colour, and passing into the state of chromic oxychloride. Chromous chloride is a powerful deoxidising agent, precipitating calomel from a solution of mercuric chloride, instantly converting tungstic acid into blue tungsten oxide, and precipitating gold from a solution of auric chloride. It forms, with ammonia, a sky-blue precipitate which turns green on exposure to the air; with ammonia and sal-ammoniac, a blue solution turning red on exposure to the air; and with ammonium sulphide, a black precipitate of chromous sulphide.

Chromic Chloride, $CrCl_3$ or Cr_2Cl_6, is obtained in the anhydrous state by heating to redness in a porcelain tube a mixture of chromium sesquioxide and charcoal, and passing dry chlorine gas over it. The trichloride sublimes, and is deposited in the cool part of the tube, in the form of beautiful crystalline plates of a pale violet colour. It is totally insoluble in water under ordinary circumstances, even boiling. It dissolves, however, and assumes the deep green hydrated state in water containing an exceedingly minute quantity of the dichloride in solution. The hydration is marked by great rise of temperature.

The green hydrated chromic chloride is easily formed by dissolving chromic hydroxide in hydrochloric acid, or by boiling lead chromate, or silver chromate, or a solution of chromic acid, with hydrochloric acid and a reducing agent, such as alcohol, or sulphurous acid, or even with hydrochloric acid alone :

$$CrO_3 + 6HCl = CrCl_3 + 3H_2O + 3Cl .$$

The solution thus obtained exhibits the same characters as the chromic oxygen-salts. When evaporated it leaves a dark-green syrup, which, when heated to 100° in a stream of dry air, yields a green mass containing $Cr_2Cl_6,9H_2O$. The same solution evaporated in a vacuum yields green granular crystals containing $Cr_2Cl_6H_2O$.

Fluorides.—*Chromic Fluoride*, CrF_3 or Cr_2F_6, is obtained by treating the dried sesquioxide with hydrofluoric acid, and strongly heating the dried mass, as a dark-green substance, which melts at a high temperature, and sublimes when still more strongly heated, in shining prisms.

Chromyl Fluoride, CrO_2F_2, is formed by distilling lead chromate with fluor-spar and fuming oil of vitriol in a leaden retort, and condensing the vapours in a cooled and dry leaden receiver. It then condenses to a blood-red fuming liquid, which volatilises when its temperature rises a few degrees higher. The vapour is red, and, when inhaled, produces violent coughing and severe oppression of the lungs. The oxyfluoride is decomposed by water, yielding hydrofluoric acid and chromium trioxide.

Oxides.—Chromium forms five oxides, containing CrO, Cr_3O_4, Cr_2O_3, Cr_3O_6, and CrO_3, the first three being analogous in composition to the three oxides of iron.

The *Monoxide*, or *Chromous Oxide*, CrO, is formed on adding potash to a solution of chromous chloride, as a brown precipitate, which speedily passes to deep foxy-red, with disengagement of hydrogen, being converted into a higher oxide. Chromous oxide forms pale blue salts, which absorb oxygen with extreme avidity. Potassio-chromous sulphate has the composition $CrK_2(SO_4)_2,6H_2O$, like the other members of the same group.

Trichromic Tetroxide, $Cr_3O_4 = CrO,Cr_2O_3$, is the above-mentioned brownish-red precipitate produced by the action of water upon the monoxide. The decomposition is not complete without boiling. This oxide corresponds with the magnetic oxide of iron, and when treated with an acid yields a mixture of chromous and chromic salts.

Sesquioxide, or *Chromic Oxide*, Cr_2O_3.—When mercurous chromate, prepared by mixing solutions of mercurous nitrate and potassium chromate, or dichromate, is exposed to a red heat, it is decomposed, pure chromium sesquioxide, having a fine green colour, remaining. In this state the oxide, like alumina after ignition, is insoluble in acids. The anhydrous sesquioxide may be prepared in a beautifully crystalline form by heating potassium pyrochromate, $K_2O,2CrO_3$, to

full redness in an earthen crucible. One-half of the chromium trioxide contained in that salt then suffers decomposition, oxygen being disengaged, and sesquioxide left. Water dissolves out from the melted mass normal potassium chromate, leaving the oxide. Chromium sesquioxide communicates a fine green tint to glass, and is used in enamel painting. From a solution of chromium sesquioxide in potash or soda, green gelatinous chromic hydroxide separates on standing. When finely powdered and dried over sulphuric acid, it consists of $Cr_2O_3,6H_2O$ or $Cr_2(HO)_6,3H_2O$. A hydroxide may also be prepared by boiling a somewhat dilute solution of potassium pyrochromate strongly acidulated with hydrochloric acid, with small successive portions of sugar or alcohol. In the former case carbon dioxide escapes: in the latter, aldehyde and acetic acid are formed, and the chromium of the salt becomes converted into chromic chloride, the colour of the liquid changing from red to deep green. The reduction may also be effected, as already observed, by hydrochloric acid alone. A slight excess of ammonia precipitates the hydroxide from its solution. It has a pale purplish-green colour, which becomes full green on ignition; a great shrinking of volume and sudden incandescence are observed when the hydroxide is decomposed by heat.

Chromium sesquioxide resembles iron sesquioxide and alumina, with which it is isomorphous; its salts (chromic salts) exist in two metameric forms, being green and amorphous or purple and crystalline.

The amorphous sulphate is produced by the action of heat upon the purple salt, and is gradually reconverted into that compound when dissolved in water.

Chromic Sulphate, $Cr_2(SO_4)_3$, is prepared by dissolving the hydroxide in dilute sulphuric acid. It unites with the sulphates of potassium and ammonium, giving rise to magnificent double salts, which crystallise in regular octahedrons of a deep claret colour, and are analogous in constitution to common alum, the aluminium being replaced by chromium. The ammonium-salt, for example, has the composition $Cr'''(NH_4)(SO_4)_2,12H_2O$. The finest crystals are obtained by spontaneous evaporation.

Chromic chromate, CrO_3,Cr_2O_3, is a brown substance obtained by digesting chromic oxide with excess of chromic acid, or by partial reduction of chromic acid with alcohol, sulphurous acid, etc.

Chromium Trioxide, CrO_3; in combination with water, forming *chromic acid*, $CrO_3,H_2O = H_2CrO_4 = (CrO_2)(OH)_2$. Whenever chromium sesquioxide is strongly heated with an alkali, in contact with air, oxygen is absorbed and the trioxide is generated. Chromium trioxide may be obtained nearly pure by mixing 100 measures of a cold saturated solution of potassium pyrochromate with 150 measures of oil of vitriol, leaving the whole to cool, pouring off the mother-liquor, and leaving the crystals to drain upon a tile, closely covered by a glass or bell-jar. Chromium trioxide crystallises in

brilliant crimson-red prisms very deliquescent and soluble in water: the solution is instantly reduced by contact with organic matter.

Chromic acid is not known except in solution. It is bibasic and analogous in composition to sulphuric acid; its salts are isomorphous with the corresponding sulphate.

Potassium Chromate, K_2CrO_4, or $(CrO_2)(OK)_2$.—This salt is made directly from the native *chrome-iron ore*, which is a compound of chromium sesquioxide and ferrous oxide, analogous to magnetic iron ore, by calcination with nitre or with potassium carbonate, or with caustic potash, the ore being reduced to powder and heated for a long time with the alkali in a reverberatory furnace. The product, when treated with water, yields a yellow solution, which, on evaporation, deposits anhydrous crystals of the same colour, isomorphous with potassium sulphate. Potassium chromate has a cool, bitter, and disagreeable taste, and dissolves in 2 parts of water at 15·5°.

Potassium Dichromate, or *Pyrochromate*, K_2CrO_4,CrO_3, analogous in composition to the pyrosulphate (p. 136), is obtained by treating the preceding salt with a moderate quantity of sulphuric acid. This salt, of which immense quantities are manufactured for use in the arts, crystallises by slow evaporation in beautiful red tabular crystals, derived from a triclinic prism. It melts when heated, and is soluble in 10 parts of water; the solution has an acid reaction.

Potassium Trichromate, $K_2O,3CrO_3$ or $K_2CrO_4,2CrO_3$, may be obtained in crystals by dissolving the dichromate in an aqueous solution of chromic acid, and leaving it to evaporate over sulphuric acid.

Lead Chromate, $PbCrO_4$.—This salt, the *chrome-yellow* of the painter, is obtained, as a brilliant yellow precipitate, on mixing solutions of potassium chromate or pyrochromate with lead nitrate or acetate. On boiling it with lime-water, one-half of the acid radicle is withdrawn, and a basic lead chromate of an orange-red colour left. The basic chromate is also formed by adding lead chromate to fused nitre, and afterwards dissolving out the soluble salts by water: the product is crystalline, and rivals vermilion in beauty of tint. The yellow and orange chrome colours are fixed upon cloth by alternate application of the chromium and lead solutions, and in the latter case by passing the dyed stuff through a bath of boiling lime-water.

Silver Chromate, Ag_2CrO_4, is precipitated as a reddish-brown powder when solutions of potassium chromate and silver nitrate are mixed. It dissolves in hot dilute nitric acid, and separates on cooling, in small ruby-red platy crystals. The chromates of *barium*, *zinc*, and *mercury* are insoluble; the first two are yellow, the last is brick-red.

Experiments.—1. Melt in an iron spoon a mixture of equal parts of nitre and potassium carbonate, and to the melted salts, whilst continuing the application of heat, add finely powdered chrome-iron stone until the mass becomes semi-solid. Let it cool, boil in water, filter, and add dilute sulphuric acid till effervescence ceases. The solution should be yellow, and when mixed with lead nitrate gives a yellow precipitate of lead chromate (mixed with sulphate), and with silver nitrate a red precipitate of silver chromate.

2. Dissolve 5 grams of potassium dichromate in 50 cubic centimetres of water; when cold, add 70 or 80 c.c. of strong sulphuric acid, mix the liquids, and let the solution cool. Small crimson needles of CrO_3 are deposited.

3. Dissolve in an evaporating dish 10 grams of potassium dichromate in 100 c.c. of water, add 10 c.c. of strong sulphuric acid, heat to boiling, and drop in gradually 13 grams of crystallised oxalic acid. Copious effervescence ensues from escape of CO_2, and the liquid becomes green. When action ceases, let the solution cool, cover the dish to exclude dust, and leave the liquid to crystallise. In the course of a few days the colour of the solution will change, and violet-coloured octahedrons of *chrome-alum* will be deposited. Compare the form of those crystals with that of common alum.

Perchromic Acid is obtained, according to Barreswil, by mixing chromic acid with dilute hydrogen dioxide, or potassium pyrochromate with a dilute but very acid solution of barium dioxide in hydrochloric acid; a liquid is then formed of a blue colour, which is removed from the aqueous solution by ether. This very unstable compound has perhaps the composition $H_2Cr_2O_8$, or Cr_2O_7,H_2O, analogous to that of permanganic acid.

Chromium Dioxydichloride, or *Chromyl Dichloride*, CrO_2Cl_2, formerly called *Chlorochromic Acid.*—When 3 parts of potassium pyrochromate and 3 parts of common salt are intimately mixed and introduced into a small glass retort, 9 parts of oil of vitriol then added, and heat applied as long as dense red vapours arise, this compound passes over as a heavy deep red liquid resembling bromine; it is decomposed by water, with production of chromic and hydrochloric acids. It is analogous to the so-called chloromolybdic, chlorotungstic, and chlorosulphuric acids in composition, and in the products which it yields when decomposed. It may be regarded as formed from the trioxide by substitution of Cl_2 for O, or from chromic acid, $(CrO_2)(OH)_2$, by substitution of Cl_2 for $(OH)_2$; also as a compound of chromium hexchloride (not known in the separate state) with chromium trioxide: $CrCl_6,2CrO_3 = 3CrO_2Cl_2$.

Trichromyl Dichloride, $(CrO_2)_3Cl_2$ or $CrO_2Cl.CrO_2.CrO_2Cl$, is formed by heating the preceding compound to 180–190° in a sealed tube: $3CrO_2Cl_2 = (CrO_2)_3Cl_2 + Cl_4$. It is a black non-crystalline powder, which deliquesces rapidly in the air to a dark reddish-brown syrupy liquid smelling of free chlorine. When gently heated in hydrogen gas it takes fire, and is resolved into chromium sesquioxide, hydrochloric acid, and water:

$$2Cr_3O_6Cl_2 + 10H = 3Cr_2O_3 + 4HCl + 3H_2O.$$

Reactions of Chromium Compounds.—A solution of chromic chloride, or a chromic oxygen salt, is not precipitated or changed in any way by hydrogen sulphide. *Ammonium sulphide* throws down

a greyish-green precipitate of chromic hydroxide. *Caustic fixed alkalis* also precipitate the hydroxide, and dissolve it easily when added in excess. *Ammonia*, the same, but nearly insoluble. The *carbonates of potassium*, *sodium*, and *ammonium* also throw down a green precipitate of hydroxide, slightly soluble in a large excess.

Chromous salts are but rarely met with; for their reactions, see Chromous Chloride, p. 496.

Chromic acid and its salts are easily recognised in solution by forming a pale yellow precipitate with *barium salts*, bright yellow with *lead salts*, brick-red with *mercurous salts*, and crimson with *silver salts;* also by their capability of yielding the green sesquioxide by reduction.

All chromium compounds, ignited with a mixture of nitre and an alkaline carbonate, yield an alkaline chromate, which may be dissolved out by water, and on being neutralised with acetic acid will give the reactions just mentioned.

The oxides of chromium and their salts, fused with borax in either blow-pipe flame, yield an emerald-green glass. The same character is exhibited by those salts of chromic acid whose bases do not of themselves impart a decided colour to the bead. The production of the green colour in both flames distinguishes chromium from uranium and vanadium, which give green beads in the inner flame only.

MOLYBDENUM.

Symbol, Mo. Atomic weight, 96.

This metal occurs in small quantity as sulphide, or *molybdenite*, and as lead molybdate, or *wulfenite*.

Metallic molybdenum has been obtained by Moissan by a process corresponding to that used in the case of chromium, using a mixture of the dioxide and a small proportion of sugar charcoal. Pure fused molybdenum is as malleable as iron, files and polishes readily, and will not scratch glass or rock crystal. Its specific gravity is 9·01. If free from carbon and silicon, it undergoes but little change in the air below a red heat; at a high temperature it burns with production of molybdic anhydride.

Molybdenum unites with carbon, and the compound, containing 9·77 to 9·90 per cent. of carbon, is very hard, and scratches steel and glass. Its specific gravity is 8·6.

Chlorides.—Molybdenum forms four chlorides, containing $MoCl_2$ or Mo_2Cl_4, $MoCl_3$ or Mo_2Cl_6, $MoCl_4$, and $MoCl_5$ or Mo_2Cl_{10}.

The *pentachloride* is produced when metallic molybdenum (previously freed from oxide by ignition in hydrogen chloride) is heated for some time in a stream of dry chlorine gas.

The pentachloride, heated to about 250° in a stream of hydrogen, is reduced to the red, difficultly volatile *trichloride*, $MoCl_3$ or Mo_2Cl_6; and this compound, heated to redness in an atmosphere of carbon dioxide free from oxygen, is resolved, according to the equation $Mo_2Cl_6 = MoCl_2 + MoCl_4$, into the yellow *dichloride* which remains in the tube, and the brown *tetrachloride* which sublimes or is carried forward by the stream of gas.

Of these four chlorides the pentachloride is the only one which crystallises distinctly, and melts and volatilises without decomposition. The pure pentachloride is black. Its vapour has a dark brown-red colour. The sulphur-yellow dichloride and the red trichloride, which is deceptively like red phosphorus, have been obtained only in the amorphous state; the tetrachloride is an indistinctly crystalline brown sublimate. In an atmosphere of carbon dioxide the dichloride bears a bright red heat without melting or volatilising; the trichloride under the same circumstances is resolved into di- and tetra-chloride, which, when again heated, splits up into pentachloride which sublimes, and trichloride which remains behind.

The di- and tri-chloride are quite permanent in the air at ordinary temperatures, and insoluble in water; the tetra- and penta-chloride, on the other hand, are extremely susceptible of the action of oxygen, and more particularly of moisture.

The dichloride is insoluble in *nitric acid*, which, however, dissolves all the other chlorides. The dichloride dissolves easily in hot *hydrochloric acid*, with aid of heat, and crystallises therefrom on cooling, in long, shining, yellow needles, $Mo_2Cl_4 3H_2O$, which give off $2H_2O$ at 100°.

The *bromides* of molybdenum correspond in composition with the chlorides; there is also an oxybromide containing $MoBr_2O_2$.

Fluorides.—Molybdenum forms three fluorides, MoF_2, MoF_4, and MoF_6, which are obtained by dissolving the corresponding oxides in hydrofluoric acid. The *hexfluoride* is not known in the free state, but only in combination with basic metallic fluorides and molybdates; thus there is a potassium salt described by Berzelius, containing $2KF, MoF_6 + K_2O, MoO_3$.

Oxides.—Molybdenum forms four oxides, MoO, Mo_2O_3, MoO_2, and MoO_3, besides several oxides intermediate between the last two, which may be regarded as molybdic molybdates.

Monoxide, MoO, is known only in the form of a black hydrate, which has been but slightly examined.

Sesquioxide, Mo_2O_3, is produced when zinc is immersed in a concentrated solution of an alkaline molybdate mixed with a quantity of hydrochloric acid sufficient to redissolve the precipitate first thrown down. The dark-coloured solution thus obtained is mixed with a large quantity of caustic potash, which precipitates a black hydrated oxide, and retains the zinc oxide in solution. The freshly precipitated hydroxide is soluble in acids and ammonium carbonate;

when heated in the air it burns to dioxide, but when dried in a vacuum it leaves the black anhydrons monoxide.

Dioxide, MoO_2, is obtained in the anhydrous state by heating molybdic trioxide in hydrogen ; or, in the hydrated state, by digesting metallie eopper in a solution of molybdie aeid in hydrochlorie aeid, until the liquid assumes a red eolour, and then adding a large exeess of ammonia. The anhydrous dioxide is deep brown, and insoluble in aeids ; the hydroxide resembles ferrie hydroxide, and dissolves in aeids, yielding red solutions. It is eonverted into molybdie aeid by strong nitrie aeid.

Trioxide, MoO_3.—To obtain this oxide (commonly ealled *molybdic acid*) native molybdennm sulphide is roasted, at a red heat, in an open vessel, and the impure molybdie trioxide thenee resulting is dissolved in ammonia. The filtered solution is evaporated to dryness, and the salt is taken up by water and purified by erystallisation. It is, lastly, deeomposed by heat, and the ammonia expelled. The trioxide may also be prepared by decomposing native lead molybdate with sulphurie aeid. It is a white erystalline powder, fusible at a red heat, and slightly soluble in water. The solution eontains *molybdic acid*, and erystals having the eomposition H_2MoO_4 are sometimes deposited from ammouium molybdate mixed with nitrie aeid. The trioxide is easily dissolved by alkalis, and forms two series of salts, viz., *normal* or *neutral molybdates*, R_2MoO_4, or R_2O,MoO_3, and *anhydromolybdates*, *bimolybdates*, or *pyromolybdates*, R_2MoO_4,MoO_3, or $R_2O,2MoO_3$, the symbol R denoting a univalent method. The neutral molybdates of the alkali metals are easily soluble in water, and their solutions yield, with the stronger aeids, a preeipitate, either of a less soluble bimolybdate, or of the anhydrous trioxide. The other molybdates are insoluble, and are obtained by preeipitation. *Lead molybdate*, $PbMoO_4$, oecurs native in yellow quadratie plates and octahedrons.

Phosphomolybdic Acid, $48MoO_3.P_4O_{10}.6H_2O.x$aq.—When an exeess of ammonium molybdate is added to an aeid solution of any phosphate a yellow preeipitate is formed which is probably variable in composition. Woleott Gibbs regards it as a derivative of the above compound, namely, as $48MoO_3.P_4O_{10}.5(NH_4)_2O.H_2O.16$aq. It is not improbable that the real amount of ammoninm present is $6NH_4$, and in that ease the formula may be simplified by dividing the whole by four :—

$$12MoO_3.(NH_4)_3PO_4.4H_2O.$$

The percentage composition represented by the two formulæ is nearly the same.

This eompound is of eonsiderable importanee, as its produetion affords the means of separating small quantities of phosphoric aeid from any aeid solution. A similar eompound is formed by arsenic acid. These eompounds are soluble in solution of ammonia, and on adding a mixture of magnesium sulphate and ammonium chloride to the liquid a preeipitate is obtained of the ammonio-magnesium phosphate or arsenate.

Sulphides.—Molybdenum forms three sulphides, MoS_2, MoS_3,

and MoS_4, the last two of which are acid sulphides, forming sulphur-salts. The *disulphide*, or *molybdic sulphide*, MoS_2, occurs native, as *molybdenite*, in crystallo-laminar masses, or tabular crystals, having a strong metallic lustre and lead-grey colour, and forming a grey streak on paper, like plumbago. The same compound is produced artificially by heating either of the higher sulphides, or by igniting the trioxide with sulphur. When roasted in contact with the air, it is converted into trioxide.

The *trisulphide*, MoS_3, is obtained by passing hydrogen sulphide into a concentrated solution of an alkaline molybdate, and precipitating with an acid. It is a black-brown powder, which is dissolved slowly by alkalis, more easily by alkaline sulphides and sulphydrates, forming sulphur-salts called *thiomolybdates*. Most of these salts have the composition R_2MoS_4, or R_2S,MoS_3, analogous to that of the molybdates. The thiomolybdates of the alkali-metals, alkaline earth-metals, and magnesium, are soluble in water, forming solutions of a fine red colour ; the rest are insoluble.

Tetrasulphide, MoS_4.—This is also an acid sulphide, forming salts called *perthiomolybdates*, the general formula of which is R_2MoS_5, or R_2S,MoS_4. The *potassium salt* is obtained by boiling the thiomolybdate with molybdenum trisulphide.

Reactions of Molybdenum Compounds.—Molybdates are usually colourless. Solutions of the alkaline molybdates yield with *acids* a precipitate of molybdic trioxide, soluble in excess of the precipitant. They are coloured yellow by *hydrogen sulphide*, from formation of a thiomolybdate of the alkali-metal, and then yield with acids a brown precipitate of molybdenum trisulphide. This is an extremely delicate test for molybdic acid.

Metallic zinc or *stannous chloride*, added to a solution of molybdic acid in hydrochloric acid, colours it blue, then green, then dark brown, in consequence of reduction. When *ortho-phosphoric acid*, or a liquid containing it, is added to the solution of ammonium molybdate, together with an excess of nitric acid, the liquid turns yellow, and after a while deposits a yellow precipitate of molybdic trioxide, combined with small quantities of phosphoric acid and ammonia. This precipitate is soluble in ammonia, and likewise in excess of the phosphate. The reaction is therefore especially adapted for the detection of small quantities of phosphoric acid. The pyrophosphates and metaphosphates do not produce the yellow precipitate. *Arsenic acid* gives a similar reaction.

All the oxides of molybdenum form, with *borax*, in the outer blow-pipe flame, a bead which is yellow while hot, and colourless on cooling ; in the inner flame a dark-brown bead, which is opaque if excess of molybdenum is present. By long continued heating the dioxide may be separated in dark-brown flakes, floating in the clear yellow glass. With *phosphorus salt* in the outer flame, all oxides of molybdenum give a bead which is greenish while hot, and colourless on cooling ; in the inner flame a clear green bead, from which molybdic oxide cannot be separated by continued heating.

TUNGSTEN, or WOLFRAM.

Symbol, W. Atomic weight, 184.

Tungsten is found, as ferrous tungstate, in the mineral *wolfram*, tolerably abundant in Cornwall; occasionally also as calcium tungstate (*scheelite* or *tungsten*), and as lead tungstate (*scheeletine*).

Tungsten, like chromium and molybdenum, has been obtained by reduction of the oxide in the electric furnace. If the oxide has been present in excess the metal is pure. It is brilliant and very hard and requires for fusion a very high temperature. Its specific gravity is 18·7.

Steel, alloyed with a small quantity of tungsten, acquires extraordinary hardness. Tungsten has also a remarkable effect on steel in increasing its power of retaining magnetism when hardened. A horse-shoe magnet of ordinary steel, weighing two pounds, is considered of good quality when it bears seven times its own weight; but, according to Siemens, a similar magnet made with steel containing tungsten may be made to carry twenty times its weight suspended from the armature.

Tungsten forms two classes of compounds, in which it is quadrivalent and sexvalent respectively, and a third class, of intermediate composition, in which it is apparently quinquivalent.

Chlorides.—These compounds are formed by heating metallic tungsten in chlorine gas. The *hexchloride*, or *tungstic chloride*, WCl_6, is also produced, together with oxychlorides, by the action of chlorine on an ignited mixture of tungstic oxide and charcoal. The oxychlorides, being more volatile than the hexchloride, may be separated from it by sublimation. The hexchloride forms dark-violet scales or fused crusts having a bluish-black metallic iridescence. By contact with water or moist air, it is converted into hydrochloric and tungstic acids. The chlorides, WCl_5, WCl_4, and WCl_2, are formed when the hexchloride is heated in hydrogen gas. The two former are crystalline: the dichloride is a loose grey powder, destitute of crystalline structure.

A *pentabromide* and *hexbromide* are formed by the action of bromine in excess on tungsten. No fluoride of tungsten has been isolated, but a number of oxyfluorides are known.

Oxides.—Tungsten forms three oxides, WO_2, WO_3, and W_2O_5, neither of which exhibits basic properties, so that there are no tungsten salts in which the metal replaces the hydrogen of an acid, or takes the electro-positive part. The trioxide exhibits decided acid tendencies, uniting with basic metallic oxides, and forming crystallisable salts called *tungstates*. The pentoxide may be regarded as a compound of the other two.

The *Dioxide*, or *Tungstous Oxide*, WO_2 or W_2O_4, is most easily pre-

pared by exposing tungstic oxide to hydrogen, at a temperature not exceeding dull redness. It is a brown powder, sometimes assuming a crystalline appearance and an imperfect metallic lustre. It takes fire when heated in the air, and burns like the metal itself, to tungstic oxide. It forms a definite compound with soda.

The *Trioxide*, or *Tungstic Oxide*, WO_3, is most easily prepared from native calcium tungstate by digestion in nitric or hydrochloric acid, the soluble calcium salt thereby produced being washed out with water, and the remaining tungstic acid ignited. From wolfram it may be prepared by repeatedly digesting the mineral in strong hydrochloric acid, ultimately with addition of a little nitric acid, to dissolve out the iron and manganese ; dissolving the remaining tungstic acid in aqueous ammonia ; evaporating to dryness ; and heating the residual ammonium tungstate in contact with the air. Tungstic oxide is a yellow powder insoluble in water, and in most acids, but soluble in alkalis. The hot solutions of the resulting alkaline tungstates, when neutralised with an acid, yield a yellow precipitate of *tungstic monohydrate* or *tungstic acid*, H_2WO_4 or H_2O,WO_3. Cold dilute solutions, on the other hand, yield with acids a white precipitate, consisting of *tungstic dihydrate*, or *hydrated tungstic acid*, $2H_2O,WO_3$ or H_2WO_4,H_2O. Tungstic acid reddens litmus and dissolves easily in alkalis.

Tungstates.—Tungstic anhydride unites with basic oxides in various and often in very unusual proportions. It is capable of existing also in two isomeric modifications, viz.—(1) *Ordinary tungstic acid*, which is insoluble in water, and forms insoluble salts with all metals, except the alkali-metals, and magnesium ; (2) *Metatungstic acid*, which is soluble in water, and forms soluble salts with nearly all metals. Ordinary tungstic acid forms normal salts containing M_2WO_4 or M_2O,WO_3, and acid salts containing $3M_2O,7WO_3$, which may perhaps be regarded as double salts composed of diacid and triacid tungstates, that is, as $2(M_2O,2WO_3)+M_2O,3WO_3$. The tungstates of potassium and sodium, especially the latter, are sometimes used as mordants in dyeing, in place of stannates ; also for rendering muslin and other light fabrics uninflammable. Tungstous tungstate, WO_2,WO_3, which has the composition of *tungsten pentoxide*, W_2O_5, is a blue substance formed by reducing tungstic oxide or tungstic acid with zinc and hydrochloric acid ; also by heating ammonium tungstate to redness in a retort.

Metatungstates.—These salts, which have the composition of quadracid tungstates, $M_2O,4WO_3$, are formed from ordinary tungstates by addition of tungstic acid, or by removing part of the basic oxide by means of an acid. They are for the most part soluble and crystallisable. By decomposing barium metatungstate with dilute sulphuric acid, and evaporating the filtrate in a vacuum, hydrated metatungstic acid is obtained in quadratic octahedrons, apparently containing $H_2W_4O_{13},31H_2O$; it is very soluble in water.

Silicotungstates.—By boiling gelatinous silica with acid potassium tungstate, a crystalline salt is obtained, having the

composition of a diacid potassium tungstate, $6(K_2O,2WO_3)$, or $K_{12}O_6,12WO_3$, in which one-third of the potassium oxide is replaced by silica, viz., $K_8SiO_6,12WO_3$, or $4K_2O.SiO_2.12WO_3$. The resulting solution yields with mercurous nitrate a precipitate of *mercurous silicotungstate*; this, when decomposed by an equivalent quantity of hydrochloric acid, yields a solution of *hydrogen silicotungstate*, or *silicotungstic acid*; and the other silicotungstates, which are all soluble, are obtained by treating the acid with carbonates.

Silicodecitungstic Acid, $H_8SiO_6,10WO_3$, or $4H_2O.SiO_2.10WO_3$, is obtained as an ammonium salt by boiling gelatinous silica with solution of acid ammonium tungstate; and from this, the acid and its other salts may be obtained in the same manner as the preceding. The silico-decitungstates are very unstable, and the acid is decomposed by mere evaporation, depositing silica, and being converted into *tungstosilicic acid*, which is isomeric with silicotungstic acid, and likewise decomposes carbonates. All three of these acids are capable of exchanging either one-half or the whole of their basic hydrogen for metals, thereby forming acid and neutral salts; silicotungstic acid also forms an acid sodium salt in which only one-fourth of the hydrogen is replaced by sodium.

Tungsten Sulphides.—The *Disulphide*, or *Tungstous Sulphide*, WS_2, is obtained in soft, black, needle-shaped crystals by igniting tungsten, or one of its oxides, with sulphur.

The *Trisulphide*, or *Tungstic Sulphide*, WS_3, is formed by dissolving tungstic acid in ammonium sulphide, and precipitating with an acid, or by adding hydrochloric acid to the solution of an alkaline tungstate saturated with hydrogen sulphide. It is a light-brown precipitate, turning black when dry. It unites easily with basic metallic sulphides, forming the *thiotungstates*, M_2WS_4, analogous to the normal tungstates.

Reactions of Tungsten Compounds.—*Hydrochloric acid*, added to solutions of ordinary tungstates, throw down a white precipitate of tungstic acid which becomes yellow on boiling and is insoluble in excess of acid; with metatungstates no precipitate is obtained. Soluble tungstates, or metatungstates, supersaturated with sulphuric, hydrochloric, phosphoric, oxalic, or acetic acid, yield, on the introduction of a piece of *zinc*, a beautiful blue colour, arising from the formation of blue tungsten oxide, W_2O_5. A soluble tungstate, mixed with *ammonium sulphide*, and then with excess of acid, yields a light-brown precipitate of tungstic sulphide soluble in ammonium sulphide. *Hydrogen sulphide* does not precipitate the acidulated solution of a tungstate, but turns it blue, owing to the formation of the blue oxide. Ordinary tungstates give, with *potassium ferrocyanide*, after addition of hydrochloric acid, a brown flocculent precipitate, soluble in pure water free from acid; metatungstates give no precipitates.

All tungsten compounds form colourless beads with borax and

phosphorus salt, in the outer blow-pipe flame. With *borax*, in the inner flame, they form a yellow glass, if the quantity of tungsten is somewhat considerable, but colourless with a smaller quantity. With *phosphorus salt* in the inner flame they form a glass of a pure blue colour, unless metallic oxides are present, which modify it ; in presence of iron the glass is blood-red, but the addition of metallic tin renders it blue.

URANIUM.

Symbol, U. Atomic weight, 239.

This metal is found in *pitchblende*, an oxide, $UO_2 2 UO_3$, which is its principal ore. It also occurs in the several minerals included under the name *uraninite*, which consist chiefly of uranate of lead, often associated with the rare metals thorium, yttrium, etc. The metal itself is isolated by decomposing the chloride with potassium or sodium, and is obtained as a black coherent powder, or in fused white malleable globules, according to the manner in which the process is conducted. It is permanent in the air at ordinary temperatures, and does not decompose water ; but in the pulverulent state it takes fire at 207°, burning with great splendour and forming a dark-green oxide. It unites also very violently with chlorine and with sulphur.

The metal in combination with carbon is obtained by reduction of the oxide in the electric furnace : it is then very hard with a brilliant fracture and melting point higher than that of platinum, but it decomposes water at the ordinary temperature.

Uranium forms two chief classes of compounds : viz., the uranous compounds, in which it is quadrivalent, *e.g.*, UCl_4, UO_2, $U(SO_4)_2$, etc., and the uranic compounds, in which it is sexvalent, *e.g.*,

$$UO_3,\ UO_2Cl_2,\ UO_2(NO_3)_2,\ UO_2(SO_4).$$

There are also two oxides intermediate between uranous and uranic oxide. There is no chloride, bromide, iodide, or fluoride corresponding with uranic oxide, such as UCl_6 : neither are there any normal uranic oxysalts, such as $U(NO_3)_6$, $U(SO_4)_3$, etc. ; but all the uranic salts contain the group UO_2, which may be regarded as a bivalent radicle (uranyl), uniting with acids in the usual proportions, and forming normal salts ; thus—

Uranic oxide or Uranyl oxide, . .	$(UO_2)O$
Uranic oxychloride or Uranyl chloride, .	$(UO_2)Cl_2$
Uranic nitrate or Uranyl nitrate, . .	$(UO_2)(NO_3)_2$
Uranic sulphate or Uranyl sulphate, .	$(UO_2)(SO_4)$.

Haloid Compounds.—*Uranous Chloride*, UCl_4, is formed, with vivid incandescence, by burning metallic uranium in chlorine gas, also by igniting uranous oxide in hydrochloric acid gas, and, lastly,

by heating uranoso-uranic oxide with charcoal in a current of chlorine. It crystallises in dark-green regular octahedrons, and dissolves easily in water, forming an emerald-green solution, which is decomposed when dropped into boiling water, giving off hydrochloric acid, and yielding a brown precipitate of hydrated uranous oxide. It is a powerful deoxidising agent, reducing gold and silver, converting ferric salts into ferrous salts, etc. Its vapour-density, determined by V. Meyer's method, was found to be 13·33 (air = 1), which agrees closely with the theoretical number 13·21 deduced from the atomic weight of uranium, 239. When heated in hydrogen gas this compound is reduced to a lower chloride, UCl_3, or more probably U_2Cl_6, a dark-brown powder.

Uranic Oxychloride, or *Uranyl Chloride*, UO_2Cl_2, is formed when dry chlorine gas is passed over red-hot uranous oxide, as an orange-yellow vapour, which solidifies to a yellow crystalline fusible mass, easily soluble in water. It forms double salts with the chlorides of the alkali-metals,—the potassium salt, for example, having the composition $UO_2Cl_2,2KCl,2H_2O$.

Uranic Chloride, UCl_5, or more probably U_2Cl_{10}, is obtained as a red crystalline substance with metallic reflection, or as a brown powder by passing chlorine gas through a heated mixture of carbon with any oxide of uranium. It is not volatile without decomposition, and hence its molecular weight has not been determined.

Uranous Bromide, UBr_4, is prepared by heating a mixture of uranoso-uranic oxide and charcoal in a current of carbon dioxide laden with bromine-vapour, and collects on the cooler parts of the tube in black glistening leaflets, which are converted by heat into a brown vapour, and may be sublimed unchanged. It is extremely hygroscopic. Vapour-density, by experiment, 19·46, by calculation, 19·36 (Zimmermann).

Fluorides.—Uranoso-uranic oxide, U_3O_8, treated with aqueous hydrofluoric acid, yields a bulky green powder consisting of uranous fluoride, UF_4, and a yellow solution which, on evaporation, leaves uranic oxyfluoride or uranyl fluoride, UO_2F_2. An isomeric compound is formed as a white sublimate when uranous fluoride is heated in the air.

Oxides.—*Uranous Oxide*, UO_2, formerly mistaken for metallic uranium, is obtained by heating the oxide, U_3O_8, or uranic oxalate, in a current of hydrogen. It is a brown powder, sometimes highly crystalline. In the finely divided state it is pyrophoric. It dissolves in acids, forming green salts.

Uranoso-uranic Oxide, $U_3O_8 = UO_2,2UO_3$.—This oxide forms the chief constituent of pitchblende. It is obtained artificially by igniting the metal or uranous oxide in contact with the air, or by gentle ignition of uranic oxide or uranic nitrate. It forms a dark-green velvety powder, of density 7·1 to 7·3. When ignited in hydrogen, or with sodium, charcoal, or sulphur, it is reduced to uranous oxide. When ignited alone, it yields a black oxide, U_2O_5. Uranoso-uranic

oxide dissolves in strong sulphuric or hydrochloric acid, yielding a mixture of uranous and uranic salt; by nitric acid it is oxidised to uranic nitrate.

Uranic Oxide, or *Uranyl Oxide*, UO_3, or UO_2O.—Uranium and its lower oxides dissolve in nitric acid, forming uranic nitrate; and when this salt is heated in a glass tube till it begins to decompose at 250°, pure uranic oxide remains in the form of a chamois-yellow powder. *Hydrated uranic oxide*, $UO_3,2H_2O$, cannot be prepared by precipitating a uranic salt with alkalis, inasmuch as the precipitate always carries down alkali with it; but it may be obtained by evaporating a solution of uranic nitrate in absolute alcohol till, at a certain degree of concentration, nitrous ether, aldehyde, and other vapours are given off, and a spongy yellow mass remains, which is the hydroxide. In a vacuum at ordinary temperatures, or at 100° in the air, it gives off half its water, leaving the *monohydrate*, UO_3,H_2O, or *uranyl dihydroxide*, $UO_2(OH)_2$. This hydrate cannot be deprived of all its water without exposing it to a heat sufficient to drive off part of the oxygen, and reduce it to uranoso-uranic oxide.

Uranic oxide and its hydrates dissolve in acids, formiug the uranic salts. The *nitrate*, $(UO_2)(NO_3)_2,6H_2O$, may be prepared from pitchblende by dissolving the pulverised mineral in nitric acid, evaporating to dryness, adding water, and filtering; the liquid yields, by due evaporation, crystals of uranic nitrate, which are purified by a repetition of the process, and, lastly, dissolved in ether. This latter solution yields the pure nitrate.

Uranates.—Uranic oxide unites with the more basic metallic oxides. The uranates of the alkali-metals are obtained by precipitating a uranic salt with a caustic alkali: those of the earth-metals and heavy metals, by precipitating a mixture of a uranic salt and a salt of the other metal with ammonia, or by igniting a double carbonate or acetate of uranium and the other metal (calcio-uranic acetate, for example) in contact with the air. The uranates have, for the most part, the composition $M_2O,2UO_3$. They are yellow, insoluble in water, soluble in acids. Those which contain fixed bases are not decomposed at a red heat; but at a white heat, the uranic oxide is reduced to uranoso-uranic oxide, or by ignition in hydrogen to uranous oxide: the mass obtained by this last method easily takes fire in contact with the air. *Sodium uranate*, $Na_2O,2UO_3$, is much used for imparting a yellowish or greenish colour to glass, and as a yellow pigment in the glazing of porcelain. The "uranium-yellow" for these purposes is prepared on the large scale by roasting pitchblende with lime in a reverberatory furnace; treating the resulting calcium uranate with dilute sulphuric acid; mixing the solution of uranic sulphate thus obtained with sodium carbonate, by which the uranium is first precipitated together with other metals, but then redissolved, tolerably free from impurity, by excess of the alkali; and treating the liquid with dilute sulphuric acid, which throws down hydrated sodium uranate, $Na_2O,2UO_3,6H_2O$. *Ammonium uranate* is but slightly soluble in pure water, and quite

insoluble in water containing sal-ammoniac; it may, therefore, be prepared by precipitating a solution of sodium uranate with that salt. It occurs in commerce as a fine deep yellow pigment, also called "uranium-yellow." This salt, when heated to redness, leaves pure uranoso-uranic oxide, and may, therefore, serve as the raw material for the preparation of other uranium compounds.

Some of the natural uranates, such as clèveite and bröggerite, have of late attracted considerable attention from the fact that, when heated alone or dissolved in acids, the mineral gives off a gas which, though originally mistaken for nitrogen, has been found by Ramsay to contain the element helium (p. 230).

Uranic oxide has also been observed by Becquerel to possess the remarkable property of emitting an invisible radiation which is capable of producing photographic effects after passing through opaque bodies, such as wood, black paper, and certain metals. The observation has been made so recently that it is not yet known whether this power is dependent upon previous exposure to light.

Peruranates.—By adding hydrogen peroxide and excess of alkali to uranic nitrate, salts are obtained which may be formulated as M'_4UO_8, corresponding to an unknown acid, H_4UO_8, and oxide, UO_6. The salts are yellow and unstable solids, which give up oxygen in contact with permanganates.

Reactions of Uranium Compounds.—Uranous salts form green solutions, from which *caustic alkalis* and *alkaline carbonates* throw down green precipitates, which dissolve in excess, especially of ammonium carbonate, forming green solutions. *Ammonium sulphide* forms a black precipitate of uranous sulphide; *hydrogen sulphide*, no precipitate.

Uranic salts are yellow, and yield with *caustic alkalis* a yellow precipitate of alkaline uranate, insoluble in excess of the reagent. *Alkaline carbonates* form a yellow precipitate, consisting of a double carbonate, soluble in excess of the alkaline carbonate. *Ammonium sulphide* forms a black precipitate of uranic sulphide. *Hydrogen sulphide* forms no precipitate, but reduces the uranic to a green uranous salt. *Potassium ferrocyanide* forms a nearly black precipitate.

All uranium compounds, fused with *phosphorus salt* or *borax* in the outer blow-pipe flame, produces a clear yellow glass, which becomes greenish on cooling. In the inner flame the glass assumes a green colour, becoming still greener on cooling. The oxides of uranium are not reduced to the metallic state by fusion with sodium carbonate on charcoal.

METALS OF THE TIN GROUP.

Titanium—Germanium—Tin—Zirconium—Cerium—Thorium.

These metals are tetrads, like silicon, forming volatile tetrachlorides; also tetrafluorides, which unite with other metallic fluorides, forming double salts analogous in composition to the silicofluorides, and generally isomorphous therewith.

Silicon exhibits none of the well-marked metallic characters shown by the majority of these elements, especially in the production by most of them of various oxysalts such as sulphates and phosphates.

Cerium has been already described in connection with the Yttrium Group, p. 449.

TITANIUM.

Symbol, Ti. Atomic weight, 48.

This is one of the rarer metals, and is never found in the metallic state. The most important titanium minerals are *rutile*, *brookite*, and *anatase*, which are different forms of titanic oxide, TiO_2, and the several varieties of *titaniferous iron*, consisting of ferrous titanate, sometimes alone, but more generally mixed with ferric or ferroso-ferric oxide. Occasionally in the slag adhering to the bottom of blast-furnaces in which iron ore is reduced, small brilliant copper-coloured cubes are found, hard enough to scratch glass, and in the highest degree infusible. This substance, of which a single smelting-furnace in the Hartz produced as much as 80 pounds, was originally believed to be metallic titanium. Wöhler, however, proved it to be a compound of titanium cyanide with titanium nitride. When these crystals are powdered, mixed with potassium hydroxide, and fused, ammonia is evolved, and potassium titanate is formed. Titanium forms several nitrides.

Metallic titanium in a finely divided state may be obtained by heating titanium and potassium fluoride with potassium.

Titanium is tetradic, like tin, and forms two classes of compounds: the titanic compounds, in which it is quadrivalent, *e.g.*, $TiCl_4$, TiO_2, and the titanous compounds, in which it is apparently trivalent, but probably also quadrivalent, *e.g.*, Ti_2Cl_6, or $Cl_3Ti.TiCl_3$.

Chlorides.—*Titanous Chloride*, Ti_2Cl_6, is produced by passing the vapour of titanic chloride mixed with hydrogen through a red-hot tube: it forms dark-violet scales having a strong lustre. *Titanic*

chloride, $TiCl_4$, is prepared by passing chlorine over an ignited mixture of titanic oxide and charcoal. It is a colourless, volatile, fuming liquid, having a density of 1·7609 at 0°, vapour-density = 6·836, and boiling at 135°. It unites very violently with water, and forms definite compounds with ammonia, ammonium chloride, hydrogen cyanide, cyanogen chloride, phosphine, and sulphur tetrachloride.

Fluorides.—*Titanous Fluoride*, Ti_2F_6, is obtained as a violet powder by igniting potassio-titanic fluoride in hydrogen gas, and treating the resulting mass with hot water. *Titanic fluoride*, TiF_4, passes over as a fuming colourless liquid, when titanic oxide is distilled with fluor-spar and fuming sulphuric acid in a platinum apparatus. It unites with hydrofluoric acid and metallic fluorides, forming double salts called titano-fluorides or fluotitanates, isomorphous with the silicofluorides, zircofluorides, etc., *e.g.*, $TiF_4,2KF$; TiF_4,CaF_2.

Oxides.—The *Sesquioxide*, or *Titanous Oxide*, Ti_2O_3, is obtained by igniting the dioxide in hydrogen, as a black powder, which, when heated in the air to a very high temperature, oxidises to titanic oxide.

The *Dioxide*, or *Titanic Oxide*, TiO_2, occurs native in three different forms, viz., as rutile and anatase, which are dimetric, and brookite, which is trimetric ; of these anatase is the purest, and rutile the most abundant. To obtain pure titanic oxide, rutile or titaniferous iron ore, reduced to fine powder, is fused with twice its weight of potassium carbonate, and the fused mass is dissolved in dilute hydrofluoric acid, whereupon titano-fluoride of potassium soon begins to separate. From the hot aqueous solution of this salt, ammonia throws down snow-white ammonium titanate, which is easily soluble in hydrochloric acid, and when ignited gives reddish-brown lumps of titanic oxide. This oxide is insoluble in water, and in all acids except strong sulphuric acid. By fusing it with six times its weight of acid potassium sulphate, a clear yellow mass is obtained, which dissolves perfectly in warm water.

Titanic oxide appears to form two hydroxides or acids, analogous to stannic and metastannic acids. One of these, called titanic acid, is precipitated by ammonia from a solution of titanic chloride, as a white powder which dissolves easily in sulphuric, nitric, and hydrochloric acids, even when these acids are rather dilute ; but these dilute solutions, when boiled, deposit metatitanic hydrate as a soft white powder, which, like the anhydrous oxide, is insoluble in all acids except strong sulphuric acid.

The titanates have not been much studied ; most of them may be represented by the formulæ $M_4TiO_4 = 2M_2O, TiO_2$, and $M_2TiO_3 = M_2O,TiO_2$ (the symbol M denoting a univalent metal). The titanates of calcium and iron occur as natural minerals. The titanates of the alkali-metals are formed by fusing titanic oxide with alkaline hydroxides, carbonates, or acid sulphates—some of them also in the

wet way. When finely pulverised and levigated, they dissolve in moderately warm, concentrated hydrochloric acid; but the greater part of the dissolved titanic acid is precipitated on boiling the solution with dilute acid. The normal titanates of the alkali-metals, M_2TiO_3, are insoluble in water, but soluble in acids. The titanates of the earth-metals and heavy metals are insoluble, and may be obtained by precipitation.

Reactions of Titanium Compounds.—From a solution of titanic acid in hydrochloric acid, alkalis throw down white gelatinous titanic acid; *potassium ferrocyanide*, a dark-brown precipitate. Zinc added to the acid solution causes the appearance of a violet coloration due to the production of titanous oxide. The most characteristic test for dissolved titanic oxide is *hydrogen dioxide*, which produces an orange or brownish coloration in the liquid.

Titanic oxide fused with borax, or better with microcosmic salt in the inner blow-pipe flame, forms a glass which is yellow while hot, but becomes violet on cooling. The delicacy of this reaction is much increased by melting a little metallic zinc in the bead.

GERMANIUM.

Symbol, Ge. Atomic weight, 72.

This element was discovered in 1886 by Winkler in a rare mineral, argyrodite, a sulphide of silver and germanium, $3Ag_2S.GeS_2$, found at Freiberg.

The metal may be reduced from the oxide by heating it with charcoal or in hydrogen. It is brittle, and crystallises in octahedrons having the specific gravity 5·47. It melts at about 900°, and is volatile.

Like the other elements of this group it forms two oxides, of which the more important is the dioxide GeO_2, and two chlorides, of which the most characteristic is the tetrachloride $GeCl_4$. It also yields a tetrethide, $Ge(C_2H_5)_4$, which boils at 160°.

Germanic Oxide, GeO_2, is produced when the metal burns in oxygen and in the hydrated state when the chloride is decomposed by water. It is a dense white powder resembling tin dioxide in many respects.

Germanic Chloride, $GeCl_4$, is produced by direct combination of germanium and chlorine, or by distilling the metal with an excess of dry mercuric chloride. It is a colourless fuming liquid, which boils at 86° and has a specific gravity 1·887 at 18°.

Germanic Fluoride, GeF_4, is known in the form of a crystalline hydrate, $GeF_4.3H_2O$, which is decomposed by heat, leaving a residue of oxide. When the vapour of the fluoride is passed into water, a solution is obtained of germanic acid and hydrofluogermanic acid,

H_2GeF_6, which yields a potassium salt soluble in about 180 parts of water at 18°.

Germanic Sulphide, GeS_2.—This compound is obtained as a white precipitate by treating an acidified solution of a germanate with hydrogen sulphide. It dissolves readily in alkaline hydrosulphides, probably with formation of thio-salts.

The atomic weight and properties of germanium show that it is identical with Mendeléeff's *ekasilicon*, occupying the position between gallium and arsenic in the periodic arrangement of the elements.

Germanium is most readily identified by the formation of the white sulphide when its alkaline solution is treated with ammonium sulphide and subsequently with a large excess of hydrochloric acid.

TIN.

Symbol, Sn (Stannum). Atomic weight, 118.

Tin has been known and used as a constituent of bronze from prehistoric times, and the Phœnicians in times antecedent to the Christian era visited Cornwall for the purpose of obtaining supplies of the metal. The principal tin mines are still those of Cornwall, but large quantities of ore are now imported from the island of Banca, in the Malay Archipelago, and from Australia.

The metal occurs in the form of oxide, as tinstone or cassiterite, SnO_2; also comparatively rarely as tin pyrites, SnS_2. In Cornwall the tinstone is found as a constituent of metal-bearing veins, associated with copper ore, in granite and slate rocks; and formerly as an alluvial deposit, mixed with rounded pebbles, in the beds of several small rivers. The first variety is called *mine-* and the second *stream-tin.* Tin oxide is also found disseminated through the rock itself in small crystals.

To prepare the ore for reduction, it is stamped to powder, washed, to separate as much as possible of the earthy matter, and roasted, to expel sulphur and arsenic: it is then strongly heated with anthracite in a reverberatory furnace similar to the furnace used in the reduction of galena. The resulting metal is very impure, and is therefore subjected to a process of *liquation.*

The bars of crude tin are exposed to a very gentle heat in a furnace similar to that employed in smelting the ore, the fusible metal drains away, whilst a mass of *hard head* remains behind consisting chiefly of iron with about 20 per cent. of tin.

Refined tin is subjected to a further process of melting, and, whilst fluid, *poling* with a green stick or *tossing* by means of a ladle.

Grain tin is produced by heating blocks of the metal to near the melting-point, and then dropping them from some height or striking with a hammer, by which the metal is broken up into columnar masses.

Pure tin has a white colour, approaching that of silver: it is soft and malleable, and when bent or twisted emits a peculiar crackling sound; its density is 7·3. At 200° it becomes so brittle that it may be powdered, and at 235° it melts. Tin is but little acted upon by air and water, even conjointly; when heated above its melting-point it oxidises rapidly, becoming converted into a whitish powder, used in the arts for polishing, under the name of *putty powder.* The metal is attacked and dissolved by hydrochloric acid, with evolution of hydrogen; nitric acid acts with great energy, converting it into a white metastannic acid.

The useful applications of tin are very numerous. *Tinned plate* consists of iron superficially alloyed with this metal. Cooking-vessels of copper are usually tinned in the interior, and pins, which are made of brass wire, are coated with tin.

The alloys of tin are especially important. *Bronze* is a mixture of copper and tin, usually associated with zinc and sometimes with lead. The bronze coinage metal of this country consists of 95 parts copper, 4 parts tin, and 1 part zinc. *Gun-metal*, *bell-metal*, and *speculum-metal* are alloys of tin and copper. The last-named is white, very hard, and takes a fine polish. *Solder* is chiefly tin containing lead; *pewter* is a mixture of tin and lead, sometimes hardened by addition of a little antimony.

Tin is also used in the form of amalgam as a backing for producing the reflecting surface of common glass mirrors.

Various soluble compounds of tin are used in dyeing and calico-printing, as will be explained later.

Tin forms two well-defined classes of compounds, namely, the stannic compounds, in which it is quadrivalent, as $SnCl_4$, SnO_2, and the stannous compounds, in which it is also quadrivalent, Sn_2Cl_4, Sn_2O_2, but which are usually represented by the simpler formulæ $SnCl_2$, SnO, as though it were bivalent.

Chlorides.—The *Dichloride*, or *Stannous Chloride*, $SnCl_2$, or more probably $Sn_2Cl_4 = Cl_2Sn{=}SnCl_2$ (vapour-density at 600–700° = 13, air = 1), is obtained in the anhydrous state by distilling a mixture of calomel and powdered tin, prepared by agitating the melted metal in a wooden box until it solidifies. It is a grey, resinous-looking substance, fusible below redness, and volatile at a high temperature.

The *hydrated chloride*, commonly called *tin salt*, is easily prepared by dissolving metallic tin in hot hydrochloric acid. It crystallises in prisms containing $SnCl_2,2H_2O$, which are freely soluble in a small quantity of water, but are partly decomposed when put into a large mass, unless hydrochloric acid be present in excess. Solution of stannous chloride is employed as a deoxidising agent; it reduces the salts of mercury and other metals of the same class. It is also extensively employed as a mordant in dyeing and calico-printing; sometimes also as antichlore.

Stannous chloride unites with the chlorides of the alkali-metals,

forming crystallisable double salts, $SnCl_2,2KCl$, etc., called *Stannoso-chlorides* or *Chlorostannites.*

The *Tetrachloride*, or *Stannic Chloride*, $SnCl_4$, formerly called *fuming liquor of Libavius*, is made by exposing metallic tin to the action of chlorine, or by distilling a mixture of 1 part of powdered tin with 5 parts of mercuric chloride. It is a thin, colourless, mobile liquid, boiling at 120°, and yielding a colourless invisible vapour. It fumes in the air, and when mixed with a third part of water, solidifies to a soft fusible mass, called *butter of tin.* The solution of stannic chloride is much employed by the dyer for the brightening and fixing of red colours, and is sometimes designated by the old names, "composition, physic, or tin solution"; it is commonly prepared by dissolving metallic tin in a mixture of hydrochloric and nitric acids, care being taken to avoid too great elevation of temperature. The solution when evaporated yields a deliquescent crystalline hydrate, $SnCl_4,5H_2O$.

Stannic chloride forms, with the chlorides of the alkali-metals and alkaline earth-metals, crystalline double salts, called *Stanno-chlorides* or *Chlorostannates, e.g.*, $SnCl_4,2NH_4Cl$, which constitutes the "pink salt" of the old-fashioned dyer. It also forms crystalline compounds with the pentachloride and oxychloride of phosphorus, viz., $SnCl_4,PCl_5$, and $SnCl_4,POCl_3$, and a solid compound with phosphine, containing $SnCl_4,2PH_3$.

Experiments.—1. Granulate about an ounce of tin by melting it in a porcelain crucible and pouring it drop by drop into cold water. Place 10 or 15 grams of the metal in a flask, pour in strong hydrochloric acid sufficient to cover it, and then add about an equal quantity of water. Apply heat. Hydrogen is given off and the metal slowly dissolves, but the action may be greatly promoted by dropping in a few scraps of platinum foil, so that they may touch the tin beneath the acid. Add a little more acid if necessary, and when the tin is dissolved pour off the solution into a dish and evaporate it to a small volume. Crystals of stannous chloride may be obtained.

2. Mix 40 c.c. of strong hydrochloric acid with 50 c.c. of water in a flask. Add 10 grams of tin, heat to boiling, and drop in gradually 10 c.c. of nitric acid. Boil till the tin is dissolved and the liquid ceases to evolve nitrous fumes. Then add 10 grams of ammonium chloride, and set the solution aside in a beaker to crystallise.

3. Suspend in a solution of stannous chloride a small piece of zinc. Crystals of tin soon make their appearance, and continue to grow as the zinc dissolves.

Fluorides.—*Stannous Fluoride*, SnF_2, or Sn_2F_4, obtained by evaporating the solution of stannous oxide in hydrofluoric acid, crystallises in small shining opaque prisms. *Stannic fluoride*, SnF_4, is not known in the free state, but unites with other metallic fluorides, forming crystalline compounds, called *stannofluorides* or *fluostannates*, isomorphous with the corresponding silicofluorides, titanofluorides,

and zircofluorides. The potassium salt contains $SnF_4,2KF,H_2O$, the barium salt, SnF_4,BaF_2, etc.

Oxides.—The *Monoxide*, or *Stannous Oxide*, SnO or Sn_2O_2, is produced by heating stannous oxalate out of contact with the air; also by igniting stannous hydrate. This *hydrate*, $2SnO.H_2O$, or $Sn_2H_2O_3, = O\langle{}^{Sn(OH)}_{Sn(OH)}$, is obtained as a white precipitate by decomposing stannous chloride with an alkaline carbonate, carbon dioxide being at the same time evolved. When carefully washed, dried, and heated in an atmosphere of carbon dioxide, it leaves anhydrous stannous oxide as a dense black powder, which is permanent in the air, but when touched with a red-hot body, takes fire and burns like tinder, producing the dioxide. The hydrate is freely soluble in caustic potash; the solution decomposes by keeping into metallic tin and dioxide. It dissolves also in sulphuric acid, forming *stannous sulphate*, $SnSO_4$, which crystallises in needles.

The *Sesquioxide*, Sn_2O_3, or $SnO.SnO_2$, is produced by the action of hydrated ferric oxide upon stannous chloride: it is a greyish, slimy substance, soluble in hydrochloric acid and in ammonia.

The *Dioxide*, or *Stannic Oxide*, SnO_2, occurs native as tinstone or cassiterite, the common ore of tin, and is easily formed by heating tin, stannous oxide, or stannous hydrate, in contact with the air. As thus prepared it is a white or yellowish amorphous powder; but by passing the vapour of stannic chloride mixed with aqueous vapour through a red-hot porcelain tube, it may be obtained in crystals. It is not attacked by acids, even in the concentrated state.

Stannic oxide forms two hydroxides, differing from one another in composition and properties; both, however, being acids, and capable of forming salts by exchanging their hydrogen for metals. These hydroxides or acids are stannic acid, SnO_2,H_2O, or H_2SnO_3 or $O{=}Sn(OH)_2$, and metastannic acid, $Sn_5O_{10}5H_2O$, or $H_{10}Sn_5O_{15}$ or $Sn_5O_5(OH)_{10}$, the former being capable of exchanging the whole of its hydrogen for metal, and forming the stannates, containing M_2SnO_3; while the latter exchanges only one-fifth of its hydrogen, forming the metastannates, $H_8M_2Sn_5O_{15}$.

Stannic acid is precipitated by acids from solutions of alkaline stannates, also from solution of stannic chloride, by calcium or barium carbonate not in excess; alkaline carbonates throw down an acid stannate. When dried in the air at ordinary temperatures it has, according to Weber, the composition $SnO_2,2H_2O$; in a vacuum half the water is given off, leaving SnO_2,H_2O.

Stannic hydroxide dissolves in the stronger acids, forming the stannic salts; thus with sulphuric acid it forms *stannic sulphate*, $Sn(SO_4)_2$ or $SnO_2,2SO_3$. *Hydrochloric acid* converts it into the tetrachloride.

Stannates.—Stannic hydroxide exhibits acid much more decidedly than basic properties. It forms easily soluble salts with the alkalis, and from these the insoluble stannates of the earth-metals and heavy

metals may be obtained by precipitation. *Sodium stannate*, Na_2SnO_3, which is much used in calico-printing as a "preparing salt" or mordant, is produced on the large scale by fusing tinstone with sodium hydrate or nitrate; by boiling the tin ore with caustic soda-solution; by fusing metallic tin with a mixture of sodium nitrate and carbonate; or by heating it with soda-solution mixed with sodium nitrate and chloride.

Metastannic acid is produced by the action of nitric acid upon tin. When dried in the air at ordinary temperatures, it contains $5SnO_2,10H_2O$ or $H_{10}Sn_5O_{15},5H_2O$, but at 100° it gives off 5 molecules of water, and is reduced to $H_{10}Sn_5O_{15}$. It is a white crystalline powder insoluble in water and in acids. It dissolves slowly in alkalis, forming the metastannates, but is gradually deposited in its original state as the solution absorbs carbonic acid from the air. The *potassium salt*, $K_2H_8Sn_5O_{15}$ or $\left.\begin{matrix}K_2O\\4H_2O\end{matrix}\right\}(SnO_2)_5$, may be precipitated in the solid state by adding pieces of solid potash to a solution of metastannic acid in cold potash. It is gummy, uncrystallisable, and strongly alkaline. The *sodium salt*, $Na_2H_8Sn_5O_{15}$, prepared in like manner, is crystallo-granular, and dissolves slowly, but completely, in water. The metastannates exist only in the hydrated state, being decomposed when deprived of their basic water.

Experiments.—1. Place a bead of metallic tin in an uncovered porcelain crucible, and heat to redness in a muffle for an hour. A yellowish infusible mass of oxide results.

2. Add to the resulting oxide three or four times its weight of potassium cyanide, and heat to fusion. Cool and dissolve out with water; a bead of tin is reproduced.

3. Boil in a flask a few grams of tin with nitric acid till completely converted into a white powder. Add water, wash and dry the insoluble powder in the steam-bath. Heat a portion with excess of solution of soda, and observe that it dissolves. If previously heated to redness, it is almost insoluble in alkali.

Sulphides.—The *Monosulphide*, SnS, or Sn_2S_2, is prepared by fusing tin with excess of sulphur, and strongly heating the product. It is a lead-grey, brittle substance, fusible at a red heat, and soluble, with evolution of sulphuretted hydrogen, in hot hydrochloric acid. A *sesquisulphide* may be formed by gently heating the above compound with a third of its weight of sulphur; it is yellowish-grey, and easily decomposed by heat. The *bisulphide*, SnS_2, or *mosaic gold*, is prepared by exposing to a low red heat, in a glass flask, a mixture of 12 parts of tin, 6 of mercury, 6 of sal-ammoniac, and 7 of flowers of sulphur. Sal-ammoniac, cinnabar, and stannous chloride sublime, while the bisulphide remains at the bottom of the vessel in the form of brilliant gold-coloured scales: it is used as a substitute for gold powder. The same compound is obtained as an amorphous light-yellow powder by passing hydrogen sulphide into a solution of stannic chloride.

Stannous salts give with:

Fixed caustic alkalis: white hydroxide, soluble in excess.

Hydrogen sulphide, . . *Ammonium sulphide*, .	black-brown precipitate of mono-sulphide, soluble in ammonium sulphide containing excess of sulphur, and reprecipitated by acids as yellow bisulphide.
Excess of caustic potash, then a little solution of *bismuth nitrate*, .	a black precipitate of bismuthous oxide, Bi_2O_2.
Mercuric chloride, . .	a white precipitate of calomel, which becomes black from reduction of mercury if the tin salt is used in excess.

Trichloride of gold, added to a dilute solution of stannous chloride, gives rise to a brownish-purple precipitate, called *purple of Cassius*. See GOLD.

Stannic salts give with:

Fixed caustic alkalis: white hydroxide, soluble in excess.
Hydrogen sulphide: yellow precipitate of bisulphide.
Ammonium sulphide: the same, soluble in excess.

Metallic zinc placed in an acid solution of any tin compound causes separation of metallic tin in spicular branching crystals (Tin tree).

ZIRCONIUM.

Symbol, Zr. Atomic weight, 90.

This metal is intermediate in many of its properties between aluminium and silicon. Its oxide, zirconia, was first obtained by Klaproth, in 1789, from zircon, which is a silicate of zirconium. It has since been found in fergusonite, eudialyte, and two or three other rare minerals.

Zirconium, like silicon, is capable of existing in the amorphous and crystalline states. These varieties are obtained by processes similar to those described for preparing the corresponding modifications of silicon (p. 214). Amorphous zirconium when heated in the air takes fire at a temperature somewhat below redness, and burns with a bright light, forming zirconia. Crystalline zirconium forms very hard brittle scales resembling antimony in colour and lustre; it burns in the air only at the temperature of the oxyhydrogen blow-pipe, but takes fire at a red heat in chlorine gas. Zirconium is but little attacked by the ordinary acids, but hydrofluoric acid dissolves it readily, with evolution of hydrogen.

Zirconium Oxides.—Besides zirconia, ZrO_2, a higher oxide (Zr_2O_5 or ZrO_3 ?) and a lower oxide (ZrO ?) are supposed to exist, but are at present very imperfectly known.

Zirconia, ZrO_2, is prepared by strongly igniting zircon (zirconium silicate) with four times its weight of dry sodium carbonate and a small quantity of sodium hydrate. The silica is separated from the fused mass by hydrochloric acid, as described in the case of berylla; the resulting solution is treated with ammonia, which throws down zirconia generally mixed with ferric oxide; the precipitate is redissolved in hydrochloric acid; and the solution is boiled with excess of sodium thiosulphate as long as sulphurous oxide continues to escape, whereby pure zirconia is precipitated, the whole of the iron remaining in the solution. Zirconia thus obtained forms a white powder, or hard lumps, of density 4·35 to 4·9. By fusing it with borax in a pottery furnace and dissolving out the soluble salts with hydrochloric acid, zirconia is obtained in small quadratic prisms isomorphous with the native oxides of tin and titanium.

Zirconium hydroxides are obtained by precipitating the solution of a zirconium salt with ammonia: the precipitate contains $ZrH_2O_3 = ZrO_2,H_2O$, or $ZrH_4O_4 = ZrO_2,2H_2O$, according to the temperature at which it is dried.

Zirconia acts both as a basic and as an acid anhydride. After ignition it is insoluble in all acids except hydrofluoric and very strong sulphuric acid, but the hydroxide dissolves easily in acids, forming the zirconium salts; the normal sulphate has the composition $Zr(SO_4)_2$, or $ZrO_2,2SO_3$.

The zirconates are obtained by precipitating a zirconium salt with potash or soda, or by igniting zirconia with an alkaline hydrate. *Potassium zirconate* dissolves completely in water. Three *sodium zirconates* have been formed, containing $Na_2ZrO_3 = Na_2O,ZrO_2$; $Na_4ZrO_4 = 2Na_2O,ZrO_2$; and $Na_2Zr_8O_{17} = Na_2O,8ZrO_2$.

Zirconium Fluoride, ZrF_4, is obtained by dissolving zirconia, or the hydroxide, in hydrofluoric acid; or in the anhydrous state, by igniting zirconia with ammonium and hydrogen fluoride till all the ammonium fluoride is driven off. It unites with other metallic fluorides, forming double salts, called zircofluorides or fluozirconates, which are isomorphous with the corresponding silicofluorides, stannofluorides, and titanofluorides, and are mostly represented by the formulæ—

$$4MF,ZrF_4\ ;\ 3MF,ZrF_4\ ;\ 2MF,ZrF_4\ ;\ MF,ZrF_4,$$

in which M denotes a monad metal. The sodium salt, however, has the composition $5NaF,3ZrF_4$.

Reactions of zirconium salts.—*Alkalis* precipitate white zirconium hydroxide, insoluble in excess of potassium hydroxide, whereby it is distinguished from aluminium and beryllium. *Potassium sulphate* gives a precipitate of double salt, $K_4Zr(SO_4)_4$, which is soluble in

hydrochloric acid, unless precipitated from a boiling solution. (Distinction from thorium and cerium.)

CERIUM.

See page 449.

THORIUM.

Symbol, Th. Atomic weight, 232.

This very rare metal was discovered in 1828 by Berzelius, in thorite, a mineral from the Norwegian island Lovön, in which it exists as a silicate. It has since been found in euxenite, pyrochlore, and a few other minerals, and recently in greater quantity in the sands of some of the North American rivers.

Metallic thorium is obtained by reducing the chloride with potassium or sodium, as a grey powder, which acquires metallic lustre by pressure, and has a density of 7·66 to 7·795. It is not oxidised by water, dissolves easily in nitric, slowly in hydrochloric acid, and is not attacked by caustic alkalis.

Thorium forms but one class of compounds, in all of which it is quadrivalent.

Thorium Oxide, or Thoria, ThO_2, is prepared by decomposing thorite with hydrochloric acid, separating the silica in the usual way, treating the filtered solution with hydrogen sulphide to separate lead and tin, and precipitating the thoria by ammonia, together with small quantities of the oxides of iron, manganese, and uranium. To get rid of these, the precipitate is redissolved in hydrochloric acid, and the hot saturated solution is boiled with a solution of normal potassium sulphate. The thorium is thereby precipitated as thorium and potassium sulphate; and from the solution of this salt in hot water, the thorium is precipitated by alkalis as a hydroxide, which, on ignition, yields pure thoria.

Thoria is white, and very heavy, its density being 9·402. After ignition it is insoluble in nitric and hydrochloric acids, and dissolves in strong sulphuric acid only after prolonged heating. The *hydroxide*, precipitated from thorium salts by alkalis, dissolves easily in acids.

Thorium Chloride, $ThCl_4$, prepared by igniting an intimate mixture of thoria and charcoal in chlorine gas, sublimes in white shining crystals. It forms double salts with the chlorides of the alkali-metals.

Thorium Sulphate, $Th(SO_4)_2$, crystallises with various quantities of water, according to the temperature at which its solution is evaporated. *Thorium and potassium sulphate,* $ThK_4(SO_4)_4,2H_2O$, separates as a crystalline powder when a crust of potassium sulphate is suspended in a solution of thorium sulphate. It is easily soluble in water, but insoluble in alcohol and in solution of potassium sulphate.

Thorium closely resembles zirconium in most of its reactions, but is distinguished by the insolubility in water and HCl of the precipitate, consisting of basic sulphate, produced by the addition of hot solution of potassium sulphate.

METALS OF THE ANTIMONY GROUP.

Vanadium.	Niobium.
Antimony.	Didymium.
Bismuth.	Tantalum.

THESE elements are pentads, the first three being obviously members of the group of which phosphorus and arsenic form the two first terms. This is especially indicated not only by the relations among their atomic weights, but by the isomorphism and close resemblance observed among many of their most characteristic compounds, as, for example, among the phosphates, arsenates, and vanadates, such as the following :—

Apatite, . . .	$3[Ca_3(PO_4)_2].CaF_2$
Pyromorphite, . .	$3[Pb_3(PO_4)_2].PbCl_2$
Mimetine, . . .	$3[Pb_3(AsO_4)_2].PbCl_2$
Vanadite, . . .	$3[Pb_3(VO_4)_2].PbCl_2$.

Arsenic, antimony, and bismuth agree in the formation of oxides, chlorides, and other compounds of corresponding composition and similar properties, allowing for differences which are necessarily connected with difference of atomic weight. The following tabular statement of the composition of the more important compounds of these three elements exhibits clearly this relationship :—

AsH_3	SbH_3	No bismuth hydride
$AsCl_3$	$SbCl_3$	$BiCl_3$
—	$SbCl_5$	—
As_4O_6	Sb_4O_6	Bi_4O_6
As_4O_{10}	Sb_4O_{10}	Bi_4O_{10}
$HAsO_3$	$HSbO_3$	$HBiO_3$
$H_4As_2O_7$	$H_4Sb_2O_7$	—
H_3AsO_4	H_3SbO_4	—
As_2S_2	—	Bi_2S_2
As_2S_3	Sb_2S_3	Bi_2S_3
As_2S_5	Sb_2S_5	—

Niobium and tantalum, notwithstanding their unquestionably quinquivalent character, as shown by their volatile pentachlorides, are about equally related to tin, titanium, and zirconium on the one side, and to molybdenum and tungsten on the other, the relationship being indicated by the formation of a considerable number of closely similar fluorides and oxyfluorides, some of which are described on a later page.

An account of didymium has been already given in connection with the rare earths (p. 451).

VANADIUM.

Symbol, V. Atomic weight, 51·1.

Vanadium is found, in small quantity, in some iron ores, also as vanadite, a lead chlorovanadate, $3Pb_3V_2O_8.PbCl_2$. It has likewise been discovered in the iron slag of Staffordshire, and in larger quantity in the copper-bearing beds at Alderley Edge and Mottram St Andrews, in Cheshire. It occurs in small quantity in some clays, and more abundantly in the ash of a lignite found near San Raphael, in the Argentine Republic.

Metallic vanadium is obtained by prolonged ignition of the dichloride in pure dry hydrogen, as a greyish-white powder, appearing under the microscope as a crystalline mass, with a strong silver-white lustre. Vanadium in combination with carbon is also obtained by reduction of the oxide in the electric furnace. Vanadium is non-volatile; decomposes water at 100°; does not tarnish in the air; burns with brilliant scintillations when thrown into a flame; burns vividly when quickly heated in oxygen, forming the pentoxide; is insoluble in hydrochloric acid; dissolves slowly in hydrofluoric acid with evolution of hydrogen, rapidly in nitric acid, forming a blue solution. In a current of chlorine it takes fire, and is converted into the tetrachloride.

Vanadium was formerly regarded as a hexad metal, analogous to tungsten and molybdenum; but Roscoe has shown that it is a pentad, belonging to the phosphorus and arsenic group. This conclusion is based upon the composition of the oxides and oxychlorides; and on the isomorphism of the vanadates with the phosphates.

Vanadium Oxides.—Vanadium forms five oxides, represented by the formulæ, V_2O, V_2O_2, V_2O_3, V_2O_4, V_2O_5, analogous, therefore, to the oxides of nitrogen.

The *Monoxide*, V_2O, is formed by prolonged exposure of metallic vanadium to the air of ordinary temperature, more quickly at a dull red heat. It is a brown substance, which, when heated in the air, is gradually converted into the higher oxides.

The *Dioxide*, V_2O_2, which was regarded by Berzelius as a metallic vanadium, is obtained by reducing either of the higher oxides with potassium, or by passing the vapour of vanadium oxytrichloride ($VOCl_3$), mixed with excess of hydrogen, through a combustion tube containing red-hot charcoal. As obtained by the second process, it forms a light-grey glittering powder, or a metallically lustrous crystalline crust, of density 3·64, brittle, very difficult to fuse, and a conductor of electricity. When heated to redness in the air,

it takes fire and burns to black oxide. It is insoluble in sulphuric, hydrochloric, and hydrofluoric acid, but dissolves easily in nitromuriatic acid, forming a dark-blue liquid.

The dioxide may be prepared in solution by the action of nascent hydrogen (evolved by metallic zinc, cadmium, or sodium-amalgam), on a solution of vanadic acid in sulphuric acid. After passing through all shades of blue and green, the liquid acquires a permanent lavender tint, and then contains the vanadium in solution as dioxide, or as hypovanadious salt. This compound absorbs oxygen more rapidly than any other known substance, and bleaches indigo and other vegetable colours as quickly as chlorine.

Vanadium dioxide may be regarded as entering into many vanadium compounds, as a bivalent radicle (like uranyl in the uranic compounds), and may therefore be called *vanadyl.*

Vanadium Trioxide, V_2O_3, or *Vanadyl Monoxide*, $(V_2O_2)''O$, is obtained by igniting the pentoxide in hydrogen gas, or in a crucible lined with charcoal. It is a black powder, with an almost metallic lustre, and infusible; by pressure it may be united into a coherent mass which conducts electricity. When exposed warm to the air, it glows, absorbs oxygen, and is converted into pentoxide. At ordinary temperatures, it slowly absorbs oxygen, and is converted into tetroxide. By ignition in chlorine gas it is converted into vanadyl trichloride and vanadium pentoxide. It is insoluble in acids, but may be obtained in solution by the reducing action of nascent hydrogen (evolved from metallic magnesium) on a solution of vanadic acid in sulphuric acid.

Vanadium Tetroxide, *Hypovanadic Oxide*, or *Vanadyl Dioxide*, $V_2O_4=(V_2O_2)O_2$.—This oxide is produced either by oxidation of the dioxide or trioxide, or by partial reduction of the pentoxide; also by heating hypovanadic chloride, $V_2O_4Cl_2$, to redness in an atmosphere of carbon dioxide. By allowing the trioxide to absorb oxygen at ordinary temperatures, the tetroxide is obtained in blue shining crystals. It dissolves in acids, the more easily in proportion as it has been less strongly ignited, forming solutions of hypovanadic salts, which have a bright-blue colour. The same solutions are produced by the action of moderate reducing agents' such as sulphurous, sulphydric, or oxalic acid, upon vanadic acid in solution; also by passing air through acid solutions of the dioxide till a permanent blue colour is attained. With the *hydrates* and *normal carbonates of the fixed alkalis*, they form a greyish-white precipitate of hydrated oxide, V_2O_4,H_2O, which dissolves in a moderate excess of the reagent, but is reprecipitated by a large excess in the form of a vanadate of the alkali-metal.

Hypovanadic Trisulphate, $V_2O_4,3SO_3+6H_2O$, is obtained as a blue deliquescent crystalline powder by dissolving vanadic oxide in strong sulphuric acid and reducing the solution with sulphurous acid. A salt of similar character, containing $4H_2O$, is obtained by precipitating the concentrated solution with strong sulphuric acid. A *disulphate*, $V_2O_4,2SO_3+7H_2O$, is obtained as a light-blue crystalline

powder, when the pure trisulphate, or the residue left on evaporating a solution of the tetroxide in sulphuric acid, is treated with absolute alcohol (Crow). Berzelius by similar means obtained a disulphate with $4H_2O$.

Vanadium tetroxide also unites with the more basic metallic oxides, forming salts called h y p o v a n a d a t e s, all of which are insoluble, except those of the alkali-metals. The solutions of the alkaline hypovanadates are brown, and when treated with *hydrogen sulphide* they acquire a splendid red-purple colour, arising from the formation of a sulphur salt.—*Acids* colour them blue, by forming a double hypovanadic salt ; *tincture of galls* colours them blackish-blue. The insoluble hypovanadates, when moistened or covered with water, become green, and are converted into vanadates.

Crow has obtained the following hypovanadates by treating hypovanadic chloride with the corresponding basic oxides :—

Potassium salt, . .	$K_2O,2V_2O_4$	$+7H_2O$
Sodium salt, . . .	$Na_2O,2V_2O_4$	$+7H_2O$
Ammonium salt, . .	$(NH_4)_2O,2V_2O_4$	$+3H_2O$
Barium salt, . . .	$BaO,2V_2O_4$	$+5H_2O$.

The *Lead Salt*, PbO,V_2O_4, is formed, together with potassium acetate and free acetic acid, by precipitating a solution of lead acetate with potassium hypovanadate :

$$K_2O,2V_2O_4 + 2Pb(C_2H_3O_2)_2 + H_2O = 2(PbO,V_2O_4) + 2KC_2H_3O_2 + 2C_2H_4O_2 .$$

The *Silver Salt*, Ag_2O,V_2O_4, is formed by a precisely similar reaction from potassium hypovanadate and silver nitrate.

Vanadium Pentoxide, *Vanadic Oxide*, or *Vanadyl Trioxide*, $V_2O_5 = (V_2O_2)O_3$.—This is the highest oxide of vanadium. It may be prepared from native lead vanadate. This mineral is dissolved in nitric acid, and the lead and arsenic are precipitated by hydrogen sulphide, which at the same time reduces the vanadium pentoxide to tetroxide. The blue filtered solution is then evaporated to dryness, and the residue digested in ammonia, which dissolves out the vanadic oxide reproduced during evaporation. Into this solution a lump of sal-ammoniac is put ; as that salt dissolves, ammonium vanadate subsides as a white powder, being scarcely soluble in a saturated solution of ammonium chloride. By exposure to a temperature below redness in an open crucible, the ammonia is expelled, and vanadic oxide left. By a similar process, Roscoe prepared vanadic oxide from a lime precipitate containing 2 per cent. of vanadium, obtained in working up a poor cobalt ore from Mottram in Cheshire.

Vanadium pentoxide has a reddish-yellow colour, and dissolves in 1000 parts of water, forming a light-yellow solution. It dissolves also in the stronger acids, forming red or yellow solutions, some of which yield crystalline compounds (vanadic salts) by spontaneous evaporation. It reacts, however, with basic oxides more readily than

with acids, forming salts called vanadates. When fused with alkaline carbonates, it eliminates 3 molecules of carbon dioxide, forming *orthovanadates* analogous to the orthophosphates; thus:

$$3(Na_2O,CO_2) + V_2O_5 = 3Na_2O,V_2O_5 + 3CO_2.$$

It also forms *metavanadates* and *pyrovanadates* analogous to the meta- and pyro-phosphates, and two series of *acid vanadates* or *anhydrovanadates*, viz.:

Lead orthovanadate,	$Pb_3(VO_4)_2$	or $3PbO,V_2O_5$
Barium pyrovanadate,	$Ba_2V_2O_7$	or $2BaO,V_2O_5$
Strontium metavanadate,	$Sr(VO_3)_2$	or SrO,V_2O_5
Strontium divanadate,	$Sr(VO_3)_2,V_2O_5$	or $SrO,2V_2O_5$
Strontium trivanadate,	$Sr(VO_3)_2,2V_2O_5$	or $SrO,3V_2O_5$.

Lead metavanadate occurs native as *dechenite*; the orthovanadate also, combined with lead chloride, as *vanadinite* or *vanadite*, $PbCl_2,3Pb_3(VO_4)_2$, the mineral in which vanadium was first discovered. *Descloizite* is a diplumbic vanadate, $Pb_2V_2O_7$, or $2PbO,V_2O_5$, analogous in composition to a pyrophosphate.

The metavanadates are mostly yellow; some of them, however, especially those of the alkaline earth-metals, and of zinc, cadmium, and lead, are converted by warming—either in the solid state, or under water, or in aqueous solution, especially in presence of a free alkali or alkaline carbonate—into isomeric colourless salts. The same transformation takes place also, though more slowly, at ordinary temperatures. The metavanadates of alkali-metal are colourless. The acid vanadates are yellow, or yellowish-red, both in the solid state and in solution: hence the solution of a neutral vanadate becomes yellowish-red on addition of an acid. The metavanadates of ammonium, the alkali-metals, barium, and lead, are but sparingly soluble in water; the other metavanadates are more soluble. The alkaline vanadates are more soluble in pure water than in water containing free alkali or salt: hence they are precipitated from their solutions by addition of alkali in excess, or of salts. The vanadates are insoluble in alcohol. The aqueous solutions of vanadates form yellow precipitates with *antimony*, *copper*, *lead*, and *mercury* salts; with *tincture of galls* they form a deep black liquid, which has been proposed for use as vanadium ink.

Hydrogen sulphide reduces them to hypovanadates, changing the colour from red or yellow to blue, and forming a precipitate of sulphur.

Ammonium sulphide colours the solutions brown-red, and, on adding an acid, a light-brown precipitate is formed, consisting of vanadic sulphide mixed with sulphur, the liquid at the same time turning blue. *Hydrochloric acid* decomposes the vanadates, with evolution of chlorine and formation of vanadium tetroxide.

Vanadium Chlorides.—Three of these compounds have been obtained, viz.: VCl_2, VCl_3, and VCl_4.

The *Tetrachloride*, VCl_4, is formed when metallic vanadium or the mononitride is heated in a current of chlorine, or when the vapour of the oxytrichloride, $VOCl_3$, mixed with chlorine, is passed several times over red-hot charcoal. It is a dark yellowish-brown liquid, having the density 1·8384 at 0°, boiling at 154°, not solidifying at 18°. Its vapour-density referred to hydrogen is 96·6, which is half the molecular weight $\left(= \frac{51·5 + 4 \times 35·4}{2}\right)$, showing that the molecule VCl_4 exhibits the normal condensation to 2 volumes of vapour. The tetrachloride is quickly decomposed by water, forming a blue solution of vanadious acid. It does not take up bromine or an additional quantity of chlorine when heated therewith in sealed tubes: hence it appears that vanadium does not readily form pentad compounds with the monad chlorous elements.

The *Trichloride*, VCl_3, is obtained by decomposition of the tetrachloride, slowly at ordinary temperatures, quickly at the boiling temperature; also by warming the trisulphide in a current of chlorine. It crystallises in peach-blossom-coloured shining plates resembling chromic chloride. It is slowly decomposed by water, forming a green solution of hypovanadic acid.

The *Dichloride*, VCl_2 or V_2Cl_4, obtained by passing the vapour of the tetrachloride mixed with hydrogen through a red-hot tube, crystallises in green micaceous plates, which are decomposed by water, forming a violet solution of hypovanadious acid.

Vanadium Oxychlorides, or Vanadyl Chlorides.—Four of these compounds are known, viz.: $VOCl_3$, $VOCl_2$, $VOCl$, and V_2O_2Cl.

The *Oxytrichloride*, $VOCl_3$ (formerly regarded as vanadium trichloride), is prepared:

1. By the action of chlorine on the trioxide:

$$3V_2O_3 + Cl_{12} = V_2O_5 + 4VOCl_3.$$

2. By burning the dioxide in chlorine gas, or by passing that gas over an ignited mixture of the trioxide, tetroxide, or pentoxide, and condensing the vapours in a cool U-tube.

Vanadium oxytrichloride, or vanadyl trichloride, is a golden-yellow liquid, of density 1·841 at 14·5°. Boiling-point, 127°. Vapour density, by experiment, 6·108; by calculation, 6·119. When exposed to the air, it emits cinnabar-coloured vapours, being resolved by the moisture of the air into hydrochloric and vanadic acids. It oxidises magnesium and sodium. Its vapour, passed over perfectly pure carbon at a red heat, yields carbon dioxide; and when passed, together with hydrogen, through a red-hot tube, it yields vanadium trioxide. These reactions show that the compound contains oxygen.

The other oxychlorides of vanadium are solid bodies obtained by partial reduction of the oxytrichloride with zinc or hydrogen.

The second, $VOCl_2$ or $V_2O_2Cl_4$ (hypovanadic chloride), is also produced by dissolving the pentoxide, with aid of heat, in hydrochloric

acid, and reducing the green solution with sulphurous acid. The resulting blue liquid leaves, on evaporation over the water-bath, a brown deliquescent residue which yields a blue solution with water (Crow).

The *Tribromide*, VBr_3, and the *Oxybromides*, $VOBr_3$, and $VOBr_2$, have also been obtained. The first is a greyish-black amorphous solid : the second a dark-red liquid ; the third a yellowish-brown deliquescent solid.

Vanadium Sulphides.—Two of these compounds are known, analogous to the tetroxide and pentoxide : both are sulphur acids. The *tetrasulphide*, or *vanadious sulphide*, V_2S_4, is a black substance formed by heating the tetroxide to redness in a stream of hydrogen sulphide ; also as a hydrate by dissolving a vanadious salt in excess of an alkaline monosulphide, and precipitating with hydrochloric acid. The *pentasulphide*, or *vanadic sulphide*, V_2S_5, is formed in like manner by precipitation from an alkaline vanadate.

Vanadium Nitrides.—The *Mononitride*, VN, is formed by heating the compound of vanadium oxytrichloride with ammonium chloride to whiteness in a current of ammonia gas. It is a greenish-white powder unalterable in the air. The *dinitride*, VN_2, or V_2N_4, is obtained by exposing the same double salt in ammonia gas to a moderate heat. It is a black powder strongly acted upon by nitric acid.

All vanadium compounds heated with borax or phosphorus-salt in the outer blow-pipe flame produce a clear bead, which is colourless if the quantity of vanadium is small, yellow when it is large ; in the inner flame the bead acquires a beautiful green colour.

Vanadic and chromic acids are the only acids whose solutions are red ; they are distinguished from one another by the vanadic acid becoming blue, and the chromic acid green by deoxidation.

When a solution of vanadic acid, or an acidulated solution of an alkaline vanadate, is shaken up with ether containing hydrogen dioxide, the aqueous solution acquires a red colour like that of ferric acetate, while the ether remains colourless. This reaction will serve to detect the presence of 1 part of vanadic acid in 40,000 parts of liquid. The other reactions of vanadium in solution have already been described.

ANTIMONY.

Symbol Sb (Stibium). Atomic weight, 120.

This important metalloid is found chiefly in the state of the black sulphide Sb_2S_3. To obtain it in the free state, the ore is freed by

fusion from earthy impurities, and is afterwards decomposed by heating with metallic iron which retains the sulphur.

Antimony has a bluish-white colour, a strong lustre, and a granular or coarsely laminated crystalline fracture, according as it is quickly or slowly cooled. By melting it in a crucible, then leaving it to cool partially, and pouring out the still liquid portion, it may be obtained in rhombohedral crystals. It is extremely brittle, and easily pulverised. Its density is 6·8. It melts just below redness, and boils and volatilises at a white heat.

On electrolysing a solution of 1 part of tartar-emetic in 4 parts of antimonious chloride with a small battery of two elements, antimony forming the positive, and metallic copper the negative pole, crusts of antimony are obtained, which possess the remarkable property of exploding and catching fire when scratched with a metal point or touched with a red-hot wire.

Antimony is not oxidised by the air at common temperatures ; but when strongly heated, it burns with a white flame, producing oxide, which is often deposited in fine crystals. It is dissolved by hot hydrochloric acid, with evolution of hydrogen and production of antimonious chloride. Nitric acid oxidises it to metantimonic acid, which is insoluble in that liquid.

Besides its application to medicine, antimony is of great importance in the arts as a constituent of several alloys. A mixture of 25 parts of antimony, 5 parts of tin, and 80 parts of lead form *type-metal.* This alloy expands at the moment of solidifying, and takes an exceedingly sharp impression of the mould. It is remarkable that its constituents shrink under similar circumstances, and make very bad castings. *Stereo-metal* is also a mixture of lead, tin, and antimony.

Britannia metal is an alloy of 9 parts tin and 1 part antimony, frequently also containing small quantities of copper, zinc, or bismuth. An alloy of 12 parts tin, 1 part antimony, and a small quantity of copper, forms a superior kind of pewter. Alloys of antimony with tin, or tin and lead, are now much used for machinery-bearings in place of gun-metal. Alloys of antimony with nickel and with silver occur as natural minerals.

Antimony forms two classes of compounds, the antimonious compounds in which it is trivalent, as $SbCl_3$, Sb_4O_6, Sb_4S_6, etc., and the antimonic compounds in which it is quinquivalent, as $SbCl_5$, Sb_2O_5, Sb_2S_5, etc.

Antimonious Hydride. Antimonetted Hydrogen. Stibine, SbH_3.—When zinc is put into a solution of antimonious oxide, and sulphuric acid added, part of the hydrogen combines with the antimony, and the resulting gas, which is a mixture of stibine with free hydrogen, burns with a greenish flame, giving rise to white fumes of antimonious oxide. When the gas is conducted through a red-hot glass tube of narrow dimensions, or burned with a limited supply of air, as when a cold porcelain surface is pressed into the flame, metallic antimony is deposited. On passing a current of anti-

monetted hydrogen through a solution of silver nitrate, a black precipitate is obtained, containing $SbAg_3$: from the formation of this compound it is inferred that the gas has the composition SbH_3, analogous to ammonia, phosphine, and arsine. There are also several analogous compounds of antimony with alcohol-radicles, such as *trimethylstibine*, $Sb(CH_3)_3$, *triethylstibine*, $Sb(C_2H_5)_3$, etc.

Chlorides.—The *Trichloride*, or *Antimonious Chloride*, $SbCl_3$, formerly called *butter of antimony*, is produced by the action of strong hydrochloric acid on antimonious sulphide and distilling the resulting solution. Antimonious chloride is a white crystalline solid which melts at 72°, and is very deliquescent: it dissolves in strong hydrochloric acid without decomposition, and the solution when poured into water gives rise to a white bulky precipitate, which, after a short time, becomes highly crystalline, and assumes a pale-fawn colour. This is the old *powder of Algaroth.* It has the composition $SbOCl$, and may be regarded as a compound of the trichloride and trioxide $SbCl_3,Sb_2O_3$. Alkaline solutions extract the chloride and leave the oxide. On heating this oxychloride, the trichloride is given off, and another oxychloride $Sb_4O_5Cl_2$ remains behind: $5SbOCl = SbCl_3 + Sb_4O_5Cl_2$. When antimonious oxide is dissolved in boiling antimonious chloride, a pearl-grey crystalline mass separates on cooling, having the composition $SbOCl,7SbCl_3$, and this when treated with absolute alcohol yields the compound $Sb_2O_3,2SbOCl$.

The *Pentachloride*, $SbCl_5$, is formed, with brilliant combustion, when finely powdered antimony is thrown into chlorine gas. It may be prepared by passing dry chlorine over pulverised antimony gently heated in a tubulated retort, or over the trichloride. It is a yellowish volatile liquid, which forms a crystalline compound with a small quantity of water, but is decomposed by a larger quantity, yielding antimonic and hydrochloric acids.

Tribromide and *Tri-iodide of Antimony* are also formed by direct combination, the reaction being attended with evolution of light and heat. The bromide sublimes in colourless deliquescent needles, melts at 95°, sublimes at 275°, and is decomposed by water, with formation of an oxybromide. The tri-iodide is a cinnabar-red powder, soluble in carbon sulphide, and crystallising therefrom in six-sided tablets.

Antimony Trifluoride, SbF_3, is obtained in rhombic pyramids by evaporating a solution of antimonious oxide in excess of hydrofluoric acid. It is deliquescent, and is soluble in water without formation of a precipitate. It forms crystalline double salts with fluorides of alkali-metals. The *pentafluoride*, SbF_5, obtained by dissolving antimonic acid in hydrofluoric acid, is a gummy mass, which is decomposed by heat. It unites with the fluorides of the alkali-metals, forming difficultly crystallisable double salts.

Oxides.—Antimony forms two oxides, Sb_4O_6 and Sb_2O_5 or Sb_4O_{10},

analogous to the chlorides, the first being a basic and the second an acid oxide, also an intermediate neutral oxide, Sb_2O_4 or Sb_4O_8.

Antimonious Oxide, Sb_4O_6, occurs native, though rarely, as *valentinite*, or *white antimony*, in shining white trimetric crystals; also as *senarmontite* in regular octahedrons: it is therefore dimorphous. It may be prepared by several methods: as by burning metallic antimony at the bottom of a large red-hot crucible, in which case it is obtained in brilliant crystals; or by pouring solution of antimonious chloride into water, and digesting the resulting precipitate with a solution of sodium carbonate. The oxide thus produced is anhydrous; it is a pale buff-coloured powder, fusible at a red heat, and volatile in a closed vessel. Its vapour density, determined at a red heat, shows that its molecular weight corresponds to the formula given above, which recalls its analogy with arsenious oxide, As_4O_6. In contact with air at a high temperature, it absorbs oxygen and becomes changed into the tetroxide. When boiled with cream of tartar (acid potassium tartrate), it is dissolved, and the solution yields on evaporation crystals of *tartar emetic*, $K(SbO)C_4H_4O_6H_2O$, which is almost the only antimonious salt that can bear admixture with water without decomposition.

An impure oxide is sometimes prepared by carefully roasting the powdered sulphide, and raising the temperature at the end of the process, so as to fuse the product: it has long been known under the name *glass of antimony*, or *vitrum antimonii*.

Antimonious oxide likewise interacts with alkalis, forming salts called *antimonites*, which, however, are very unstable.

The *Tetroxide*, or *Antimonoso-Antimonic Oxide*, Sb_2O_4 or more probably Sb_4O_8, Sb_2O_3, Sb_2O_5, occurs native as *cervantite*, or *antimony ochre*, in acicular crystals, or as a crust or powder. It is the ultimate product of the oxidation of the metal by heat and air: it is a greyish-white powder, infusible and non-volatile, insoluble in water and acids, except when recently precipitated. On treating it with tartaric acid or acid potassium tartrate, antimonious oxide is dissolved, antimonic acid remaining behind; and when a solution of the tetroxide in hydrochloric acid is gradually dropped into a large quantity of water, antimonious oxide is precipitated, while antimonic acid remains dissolved. From these and similar reactions it has been inferred that the tetroxide is a compound of the trioxide and pentoxide. On the other hand, it is sometimes regarded as a distinct oxide, because it dissolves in alkalis, forming salts (often called *antimonites*) which may be obtained in the solid state. Two potassium salts, for example, have been formed, containing K_2O,Sb_2O_4 and $K_2O,2Sb_2O_4$; and a calcium salt, $3CaO,2Sb_2O_4$, occurs as a natural mineral, called *romeine*. These salts may, however, be regarded as compounds of antimonates and antimonites: thus,

$$2K_2O,Sb_4O_8 = K_2O,Sb_2O_5 + K_2O,Sb_2O_3, \text{ or } 2KSbO_3 + 2KSbO_2.$$

Antimonic Oxide, Sb_2O_5, is formed as an insoluble hydrate or

hydroxide when strong nitric acid is made to act upon metallic antimony; or by decomposing antimony pentachloride with an excess of water, hydrochloric acid being formed at the same time. On exposing these hydrates to a temperature short of redness, it yields the anhydrous pentoxide as a pale straw-coloured powder, insoluble in water and acids. It is decomposed by a red heat, yielding the tetroxide and oxygen gas.

The hydroxides or antimonic acids produced by the two processes mentioned, differ in many of their properties, and especially in their deportment with bases. The acid produced by nitric acid, called antimonic acid, or *metantimonic acid*, is monobasic, producing normal salts of the form M_2O,Sb_2O_5 or $MSbO_3$, and acid salts, containing $M_2O,2Sb_2O_5$ or $2MSbO_3,Sb_2O_5$. The other, often called metantimonic acid, but more appropriately *pyroantimonic acid*, forms salts containing $2M_2O,Sb_2O_5$ or $M_4Sb_2O_7$, and acid salts containing $2M_2O,2Sb_2O_5$ or M_2O,Sb_2O_5, so that the acid pyroantimonates are isomeric or polymeric with the normal metantimonates. Among the pyroantimonates an acid potassium salt, $K_2H_2Sb_2O_7.6H_2O$, is to be particularly noticed as yielding a precipitate with sodium salts: it is, indeed, the only reagent which precipitates sodium. It is obtained by fusing antimonic oxide with an excess of potash in a silver crucible, dissolving the fused mass in a small quantity of cold water, and allowing it to crystallise in a vacuum. The crystals consist of normal potassium pyroantimonate, $K_4Sb_2O_7$, and, when dissolved in pure water, are decomposed into free potash and acid pyroantimonate. Orthoantimonates are unknown, but the precipitate formed by decomposing the pentachloride with water probably consists of *orthoantimonic acid*, H_3SbO_4.

Sulphides.—The *Trisulphide*, or *Antimonious Sulphide*, Sb_2S_3, occurs native as a black, brittle substance, having a radiated crystalline texture, and easily fusible. It may be prepared artificially by melting together antimony and sulphur. When a solution of tartar-emetic is precipitated by hydrogen sulphide, an orange-red precipitate falls, which is the same substance combined with a little water. If the precipitate be dried and gently heated, the water may be expelled without other change of colour than a little darkening, but at a higher temperature it assumes the colour and aspect of the native sulphide. This remarkable change probably indicates a passage from the amorphous to the crystalline state. When powdered antimonious sulphide is boiled in a solution of caustic potash, it is dissolved, antimonious oxide and potassium sulphide being produced; the former remains in solution as potassium antimonite, and the latter unites with an additional quantity of antimonious sulphide to form a soluble thio-salt:

$$6KHO + Sb_2S_3 = K_3SbO_3 + K_3SbS_3 + 3H_2O.$$

The antimonious oxide separates in small crystals from the boiling solution when the latter is concentrated, and the sulphur-salt dis-

solves an extra portion of antimonious sulphide, which it again deposits on cooling as a red amorphous powder, containing a small admixture of antimonious oxide and potassium sulphide. This is the *kermes mineral* of the old chemists. The filtered solution mixed with an acid gives a potassium salt, hydrogen sulphide, and precipitated orange-red antimonious sulphide. Kermes may also be made by fusing a mixture of 5 parts antimonious sulphide and 3 of dry sodium carbonate, boiling the mass in 80 parts of water, and filteiing while hot: the compound separates on cooling. The compounds of antimonious sulphide with metallic sulphides are called *thioantimonites*; many of them occur as natural minerals. For example: zinkenite, PbS,Sb_2S_3; feather-ore, $2PbS,Sb_2S_3$; boulangerite, $3PbS,Sb_2S_3$; fahlore, or tetrahedrite, $4Cu_2S,Sb_2S_3$, the antimony being more or less replaced by arsenic, and the copper by silver, iron, zinc, and mercury.

Antimony trisulphide enters into the composition of the blue or Bengal lights used at sea, which contain: dry nitre 6 parts, sulphur 2 parts, antimony trisulphide 1 part; all in fine powder and intimately mixed.

The *Pentasulphide*, or *Antimonic Sulphide*, Sb_2S_5, formerly called *sulphur auratum*, is also a sulphur-anhydride, forming salts called *thioantimonates*, most of which have the composition $3M_2S,Sb_2S_5$ or M_3SbS_4, analogous to the normal orthophosphates and arsenates. When finely powdered antimonious sulphide, with about one-fifth of its weight of sulphur, is boiled in solution of caustic soda till dissolved, the following reaction occurs :—

$$Sb_2S_3 + S_2 + 8NaHO = Na_3SbO_4 + Na_3SbS_4 + Na_2S + 4H_2O.$$

This solution, mixed with dilute sulphuric acid, furnishes sodium sulphate, and antimony pentasulphide, which falls as a golden-yellow flocculent precipitate, the *antimonium sulphuratum* of the Pharmacopœia.

The thioantimonates of the alkali-metals and alkaline earth-metals are very soluble in water, and crystallise for the most part with several molecules of water. Those of the heavy metals are insoluble, and are obtained by precipitation.

Experiments.—1. Boil in a pint retort 2 ounces of finely powdered native sulphide of antimony with about half a pint of strong hydrochloric acid till dissolved. The experiment must be made in a fume chamber. Continue to boil till the liquid is reduced to about one-half. A flask may then be added as receiver, and when the condensed product begins to crystallise in the neck of the retort, which should be kept cool by means of wet filter paper, the receiver may be changed and the distillation continued. Preserve the product in a sealed glass tube or stoppered bottle.

2. Pour the acid liquid collected in the first receiver into several times its volume of water, let the precipitated oxychloride subside completely, then siphon off the water. Stir up the precipitate with solution of sodium carbonate, let it again subside, collect the precipitate on a filter, and wash with water.

3. Place the moist oxide prepared in Experiment 2 in a dish with rather more than an equal quantity of acid tartrate of potassium. Boil up with water till the whole is dissolved, and crystallise out the tartar-emetic.

4. Pass sulphuretted hydrogen into a solution of antimonious chloride, filter off the precipitated orange sulphide, wash it, and dry in the steam-oven. When dry, heat a portion in a test-tube filled with carbon dioxide to about the melting-point of tin. The sulphide then gives off a little water, and suddenly becomes black and crystalline.

Reactions of Antimony Compounds.—The few salts of antimony soluble in water are distinctly characterised by the orange or brick-red precipitate with *hydrogen sulphide*, which is soluble in a solution of ammonium sulphide, and again precipitated by an acid.

Antimonious chloride, as already observed, is decomposed by *water*, yielding a precipitate of oxychloride. The precipitate dissolves in hydrochloric acid, and the resulting solution gives, with *potash*, a white precipitate of trioxide, soluble in a large excess of the reagent. If, however, the solution contains *tartaric acid*, the precipitate formed by potash dissolves easily in excess of the alkali, forming tartar-emetic (potassio-antimonious tartrate). *Zinc*, in contact with platinum foil, precipitates antimony from its solutions as a black powder, which is deposited upon the foil. *Copper*, boiled in an acidified solution of an antimonious compound, becomes covered with a shining metallic film, which, when heated alone in a small tube, gives no sublimate of crystals (distinction from arsenic).

For the detection of small quantities of antimony, Marsh's test (see Arsenic, p. 190) may be employed. The metal may be separated from the gaseous hydride either (1) by passing through a heated tube, when a black specular deposit is formed; (2) by burning the gas and holding a porcelain dish in the flame, when black spots are obtained insoluble in sodium hypochlorite; or (3) by passing the gas into solution of silver nitrate, when a black precipitate of silver antimonide, Ag_3Sb, is formed.

Solid antimony-compounds, fused upon charcoal with sodium carbonate or potassium cyanide, yield a brittle globule of antimony, a thick white fume being at the same time given off, and the charcoal covered to some distance around with a white deposit of oxide.

BISMUTH.

Symbol, Bi. Atomic weight, 208.

Bismuth is found chiefly in the metallic state disseminated through various rocks, from which it may be separated by simple fusion. It occurs as the trioxide or *bismuth ochre*, Bi_2O_3, less frequently as *bismuthite*, Bi_2S_3, and still more sparingly in a few other minerals, as *tetradymite* or *telluric bismuth*, Bi_2Te_3, *eulytin* or bismuth silicate, etc.

Extraction.—The chief sources of bismuth are the Saxon smalt-works, where ores containing bismuth and cobalt are worked. Formerly the bismuth was extracted by simply heating these ores in sloping tubes; but in this way only the portion existing in the metallic state was obtained, and not the whole even of that. The residue was used in the preparation of smalt, and the bismuth again extracted from the cobalt-speiss. At present, however, all bismuth ores are roasted, and afterwards smelted in the pots of the smalt furnaces, with addition of iron, carbon, and slag. Two layers are thus obtained, the lower consisting of nearly pure bismuth, which, owing to its low melting-point, can be drawn off in the liquid state after the upper layer of cobalt-speiss has solidified. The crude bismuth thus obtained contains small quantities of iron, cobalt, lead, and arsenic, from which it may be purified by fusion with nitre. A considerable quantity of bismuth from various parts of the world is now worked up in England at the Magnesium Works at Patricroft.

Bismuth is highly crystalline and very brittle; it has a greyish-white colour, with distinct reddish tinge, its density is 9·823 at 12°, and it melts at 270°, expanding in the act of solidification. It may be obtained in very fine crystals by melting a considerable quantity, leaving it to cool till it begins to solidify, then piercing the crust, and pouring out the liquid residue. The crystals thus obtained are rhombohedrons with angles of nearly 90°, so that they present the appearance of cubes. Bismuth volatilises at a high temperature. It is remarkable as being the most diamagnetic of all known bodies. It is little oxidised by the air, but burns with a bluish flame when strongly heated. Nitric acid somewhat diluted dissolves it freely.

A mixture of 8 parts of bismuth, 5 parts of lead, and 3 of tin is one of several mixtures known under the name of *fusible metal*, and is employed in taking impressions from dies and for other purposes: it melts below 100°.

Bismuth is used, in conjunction with antimony, in the construction of thermo-electric piles, these two metals forming the opposite extremes of the thermo-electric series.

Bismuth forms three classes of compounds, of which those in which it is trivalent are the most stable and the most numerous. The only known compounds in which bismuth is quinquivalent are indeed the pentoxide, Bi_2O_5, together with the corresponding metallic salts. Nevertheless, bismuth is regarded as a pentad, on account of the analogy of its compounds with those of antimony. Several bismuth compounds are known in which the metal is apparently bivalent, but really trivalent, as:

$$Bi_2Cl_4, \text{ or } \begin{array}{l} BiCl_2 \\ | \\ BiCl_2 \end{array}; \quad Bi_2O_2, \text{ or } \begin{array}{l} Bi{=}O \\ | \\ Bi{=}O \end{array}, \text{ etc.}$$

Chlorides.—The *Trichloride*, or *Bismuthous Chloride*, is formed when bismuth is heated in a current of chlorine gas, and sublimes as a white, easily fusible, volatile substance melting at 225°, which

readily attracts moisture from the air, and is converted into a crystallised hydrate. The same substance is produced when bismuth is dissolved in nitromuriatic acid, and the solution evaporated. Bismuthous chloride dissolves in water containing hydrochloric acid, but is decomposed by pure water, yielding a white precipitate of oxychloride :

$$BiCl_3 + H_2O = BiClO + 2HCl.$$

The *Dichloride*, Bi_2Cl_4, produced by heating the trichloride with metallic bismuth, is a brown, crystalline, easily fusible mass, decomposed by water. At a high temperature it is resolved into the trichloride and metallic bismuth.

Oxides.—*Hypobismuthous Oxide*, Bi_2O_2, is obtained, as a black precipitate, when a mixture of bismuthous and stannous chlorides is poured into excess of solution of potash. The precipitate must be washed and dried, while protected as much as possible from contact with air, as it is very easily oxidisable.

The *Trioxide*, or *Bismuthous Oxide*, Bi_2O_3, is a straw-yellow powder, obtained by gently igniting the neutral or basic nitrate. It is fusible at a high temperature, and in that state acts towards siliceous matter as a powerful flux.

The *Hydroxide*, Bi_2O_3,H_2O, or $BiO(HO)$, is obtained as a white precipitate when a solution of the nitrate is decomposed by an alkali. Both the hydroxide and the anhydrous oxide dissolve in the stronger acids, forming the bismuthous salts, which have the composition BiR_3, where R denotes an acid radicle, *e.g.*, $BiCl_3$, $Bi(NO_3)_3$, $Bi_2(SO_4)_3$. Many of these salts crystallise well, but cannot exist in solution unless an excess of acid is present. On diluting the solutions with water, a basic salt is precipitated, and an acid salt remains in solution.

Bismuth Pentoxide, or *Bismuthic Oxide*, Bi_2O_5.—When bismuth trioxide is suspended in a strong solution of potash, and chlorine passed through the liquid, decomposition of water ensues, hydrochloric acid being formed, and the trioxide being converted into the pentoxide. To separate any trioxide that may have escaped oxidation, the powder is treated with dilute nitric acid, when the bismuthic oxide is left as a reddish powder, which is insoluble in water. This substance combines with bases, but the compounds are not very well known. According to Arppe, there is an acid potassium bismuthate containing $KHBi_2O_6$, or $K_2H_2Bi_2O_7.Bi_2O_5$. The pentoxide when heated loses oxygen, an intermediate oxide, Bi_2O_4, being formed, which may be considered as *bismuthous bismuthate*, $2Bi_2O_4 = Bi_2O_3,Bi_2O_5$.

Oxysalts.—The *Normal Nitrate*, $Bi(NO_3)_3,5H_2O$, forms large transparent colourless crystals, which are decomposed by water in the manner just mentioned, yielding an acid solution containing a little bismuth, and a brilliant white crystalline powder, which varies to a certain extent in composition according to the temperature and

the quantity of water employed, but usually consists of a hydroxy-nitrate $Bi(NO_3)(OH)_2$. A solution of bismuth nitrate, free from any great excess of acid, poured into a large quantity of cold water, yields an insoluble basic nitrate, very similar in appearance to the above, but containing rather a larger proportion of bismuth oxide. This basic nitrate was once extensively employed as a cosmetic, but it is said to injure the skin, rendering it yellow and leather-like. It is used in medicine.

Reactions of Bismuth Salts.—Bismuth is characterised by the decomposition of its nitrate, and especially its chloride, by *water*, with production of a white milkiness which disappears on addition of sufficient acid; also by the formation of a black precipitate of suboxide, Bi_2O_2, on mixing the solution of a bismuth salt with *stannous chloride* previously mixed with excess of caustic potash. Bismuth sulphide, Bi_2S_3, is formed when *hydrogen sulphide* is passed into an acid solution, as a black precipitate which is insoluble in ammonium sulphide. Bismuth chromate (an oxysalt, $xBi_23CrO_4yBi_2O_3$) is a yellow precipitate insoluble in potash produced by the addition of a soluble chromate to a slightly acid solution of bismuth.

NIOBIUM.

Symbol, Nb. Atomic weight, 94.

This metal, discovered in 1801 by Hatchett, in American columbite, exists likewise, associated with tantalum, in columbites from other sources, and in most tantalites; also associated with yttrium, uranium, iron, and small quantities of other metals, in Siberian samarskite, uranotantalite, or yttroilmenite; also in pyrochlore, euxenite, and a variety of pitchblende from Sätersdalen in Norway.

The metal, obtained in the same manner as tantalum, is a black powder, which oxidises with incandescence when heated in the air. It dissolves in hot hydrofluoric acid, with evolution of hydrogen, and, at ordinary temperatures, in a mixture of hydrofluoric and nitric acid; slowly also when heated with strong sulphuric acid. It is oxidised by fusion with acid potassium sulphate, and gradually converted into potassium niobate by fusion with potassium hydrate or carbonate.

Niobium is quinquivalent, and forms only one class of compounds, namely, a chloride, $NbCl_5$; oxide, Nb_2O_5; oxychloride, $NbOCl_3$.

Niobic Oxide, Nb_2O_5, is formed when the metal burns in the air. It is prepared from columbite, etc., by fusing the levigated mineral in a platinum crucible with 6 or 8 parts of acid potassium sulphate, removing soluble salts by boiling the fused mass with water, digesting the residue with ammonium sulphide to dissolve tin and tung-

sten, boiling with strong hydrochloric acid to remove iron, uranium, and other metals, and finally washing with water. As thus obtained, it is generally mixed with tantalic oxide, from which it may be separated by means of hydrogen-potassium fluoride, which converts the tantalum into sparingly soluble potassium tantalofluoride, $3KF,TaF_5$, and the niobium into easily soluble potassium nioboxyfluoride, $2KF,NbOF_3+H_2O$.

Niobic oxide is a white amorphous infusible powder, having a density 4·53 and becoming crystalline when strongly heated. By fusion with boric oxide or with borax, it may be obtained in prismatic crystals.

Niobium Hydroxide, or *Niobic Acid*, $HNbO_3$, formed by decomposing the pentachloride or oxychloride with water, is a white powder resembling tantalic acid in its principal properties. It is slightly soluble in hot hydrochloric acid, and the solution, on addition of zinc, turns blue and yields a precipitate, probably of Nb_2O_4.

Niobates.—Some of these salts occur as natural minerals, columbite, for example, being a ferromanganous niobate. The *potassium niobates* crystallise readily and in well-defined forms. The *hexniobate*, $K_8Nb_6O_{19},16H_2O$ or $4K_2O,3Nb_2O_5,16H_2O$, obtained by fusing niobic oxide with twice its weight of potassium carbonate dissolving the melt in water, and evaporating under the air-pump, forms large glistening monoclinic crystals which effloresce on exposure to the air. On adding caustic potash to the solution of this salt, and evaporating slowly, the salt $K_6Nb_4O_{13},13H_2O$ is obtained in efflorescent rhombic pyramids. By fusing niobic oxide and potassium carbonate together in molecular proportions, a crystalline mass is obtained which when treated with water yields the salt,

$$2K_2Nb_4O_{11},11H_2O \text{ or } 2(K_2O,2Nb_2O_5) + 11H_2O.$$

With a larger proportion of potassium carbonate the salt

$$K_4Nb_6O_{17},11H_2O \text{ or } 2K_2O,3Nb_2O_5 + 11H_2O$$

is obtained. The *sodium niobates* are crystalline powders which decompose during washing. There is also a sodium and potassium niobate containing $Na_2O,3K_2O,3Nb_2O_5,9H_2O$.

Niobic Chloride, $NbCl_5$, is obtained, together with the oxychloride, by heating an intimate mixture of niobic oxide and charcoal in a stream of chlorine gas. It is yellow, volatile, and easily fusible. Its observed vapour-density, according to Deville and Troost, is 9·6 referred to air, or 138·6 referred to hydrogen as unity; by calculation for a two-volume condensation, it is $\frac{94+5.35\cdot5}{2} = 135\cdot75$. The *oxychloride*, $NbOCl_3$, is white, volatile, but not fusible: its density, referred to hydrogen, is by observation, 114·06: by calculation, $\frac{94+16+3.35\cdot5}{2} = 108\cdot25$. Both these compounds are converted by water into niobic oxide.

Niobic Oxyfluoride, $NbOF_3$, is formed by dissolving niobic oxide in hydrofluoric acid. It unites with the fluorides of the more basic metals, forming salts isomorphous with the titanofluorides, stannofluorides, and tungstofluorides, 1 atom of oxygen in these salts taking the place of 2 atoms of fluorine. Marignac has obtained five potassium nioboxyfluorides, all perfectly crystallised, namely :

$2KF,NbOF_3,H_2O$,	crystallising in	monoclinic plates,
$3KF,NbOF_3$,	,,	cuboïd forms (system undetermined),
$3KF,HF,NbOF_3$,	,,	monoclinic needles,
$5KF,3NbOF_3,H_2O$,	,,	hexagonal prisms,
$4KF,3NbOF_3,2H_2O$,	,,	triclinic prisms.

Potassium Niobofluoride, $3KF,NbF_5$, separates in shining monoclinic needles from a solution of the first of the above-mentioned nioboxyfluorides in hydrofluoric acid. Nioboxyfluorides of ammonium, sodium, zinc, and copper have also been obtained.

The isomorphism of these salts with the stannofluorides, titanofluorides, and tungstofluorides, shows clearly that the existence of isomorphism between the corresponding compounds of any two elements must not be taken as a decided proof that those elements are of equal valency, for in the case now under consideration, we have isomorphous salts formed by tin and titanium which are tetrads, niobium which is a pentad, and tungsten which is a hexad.

The compounds of niobium cannot easily be mistaken for those of any other metal except tantalum. The most characteristic reactions of niobates and tantalates with liquid reagents are the following :—

	Niobates.	*Tantalates.*
Hydrochloric acid, . .	White precipitate, insoluble in excess.	White precipitate, soluble in excess.
Ammonium chloride, .	Precipitation slow and incomplete.	Complete precipitation as acid ammonium tantalate.
Potassium ferrocyanide,	Red precipitate.	Yellow precipitate.
,, ferricyanide,	Bright-yellow precipitate.	White precipitate.
Infusion of galls, . .	Orange-red precipitate.	Light-yellow precipitate.

Niobic oxide, heated with borax in the outer blow-pipe flame, forms a colourless bead, which, if the oxide is in sufficient quantity, becomes opaque by interrupted blowing or flaming. In microcosmic salt it dissolves abundantly, forming a colourless bead in the outer

flame, and in the inner a violet-coloured, or if the bead is saturated with the oxide, a beautiful blue bead, the colouring disappearing in the outer flame.

DIDYMIUM.

See page 451.

TANTALUM.

Symbol, Ta. Atomic weight, 182.

This metal was discovered, in 1803, by Ekeberg, in two Swedish minerals, tantalite and yttrotantalite. A very similar metal, *columbium*, had been discovered in the preceding year by Hatchett, in columbite from Massachusetts; and Wollaston, in 1807, on comparing the compounds of these metals, concluded that they were identical, an opinion which was for many years received as correct; but their separate identity was completely established by the researches of H. Rose (commenced in 1846), who gave to the metal from the American and Bavarian columbites, the name *Niobium*, by which it is now universally known. More recently, Marignac showed that nearly all tantalites and columbites contain both tantalum and niobium (or columbium), some tantalates, from Kimito, in Finland, being, however, free from niobium, and some of the Greenland columbites containing only the latter metal unmixed with tantalum. In all these minerals tantalum exists as a tantalate of iron and manganese; yttrotantalite is essentially a tantalate of yttrium, containing also uranium, calcium, iron, and other metals. Tantalum is also contained in some varieties of wolfram.

Metallic tantalum is obtained by heating the fluotantalate of potassium or sodium with metallic sodium in a well-covered iron crucible, and washing out the soluble salts with water. It is a black powder, which, when heated in the air, burns with a bright light, and is converted, though with difficulty, into tantalic oxide. It is not attacked by sulphuric, hydrochloric, nitric, or even nitromuriatic acid. It dissolves slowly in warm aqueous hydrofluoric acid, with evolution of hydrogen, and very rapidly in a mixture of hydrofluoric and nitric acids.

Tantalum, in its principal compounds, is quinquivalent, the formula of tantalic chloride being $TaCl_5$, that of tantalic fluoride, TaF_5, and that of tantalic oxide (which, in combination with basic oxides, forms the tantalates), Ta_2O_5. There is also a tantalous oxide, said to have the composition TaO_2, and a corresponding sulphide, TaS_2.

Tantalic Chloride, $TaCl_5$, is obtained, as a yellow sublimate, by igniting an intimate mixture of tantalic oxide and charcoal in a

stream of chlorine gas. It begins to volatilise at 144°, and melts to a yellow liquid at 221°. The vapour-density between 350° and 440° has been found by Deville and Troost to be 12·42 referred to air, or 178·9 referred to hydrogen : by calculation, for the normal condensation to two volumes, it is 179·75. Tantalic chloride is decomposed by water, yielding hydrochloric and tantalic acids ; but the decomposition is not complete even at the boiling temperature.

Tantalic Fluoride, TaF_5, is obtained in solution by treating tantalic hydroxide with aqueous hydrofluoric acid. The solution, mixed with alkaline fluorides, forms soluble crystallisable salts, called tantalofluorides, or fluotantalates. The potassium salt, TaK_2F_7 or $TaF_5,2KF$, crystallises in monoclinic prisms, isomorphous with the corresponding fluoniobate.

Tantalic Oxide, Ta_2O_5, is produced when tantalum burns in the air, also by the action of water on tantalic chloride, and may be separated as a hydroxide from the tantalates by the action of acids. It may be prepared from tantalite, which is a tantalate of iron and manganese, by fusing the finely pulverised mineral with twice its weight of potassium hydroxide, digesting the fused mass in hot water, and supersaturating the filtered solution with hydrochloric or nitric acid : tantalic hydroxide is then precipitated in white flocks, which may be purified by washing with water.

Anhydrous tantalic oxide, obtained by igniting the hydroxide or sulphate, is a white powder, varying in density from 7·022 to 8·264, according to the temperature to which it has been exposed. Heated in ammonia gas it yields tantalum nitride : heated with carbon bisulphide, it is converted into tantalum bisulphide. It is insoluble in all acids, and can be rendered soluble only by fusion with potassium hydroxide or carbonate.

Tantalum Hydroxide, or *Tantalic Acid*, obtained by precipitating an aqueous solution of potassium tantalate with hydrochloric acid, or by decomposing the chloride with water, is a snow-white bulky powder, which dissolves in hydrochloric and hydrofluoric acids ; when strongly heated, it glows and gives off water.

Tantalic oxide unites with basic metallic oxides, forming the tantalates, which are represented by the formulæ, M_2O,Ta_2O_5 and $4M_2O,3Ta_2O_5$, the first including the native tantalates, such as ferrous tantalate, and the second certain easily crystallisable tantalates of the alkali-metals. The tantalates of the alkali-metals are soluble in water, and are formed by fusing tantalic oxide with caustic alkalis : those of the earth metals and heavy metals are insoluble, and are formed by precipitation.

Tantalum Dioxide, or *Tantalous Oxide*, TaO_2, may be represented by the formula $\begin{array}{c} O{=}Ta{=}O \\ | \\ O{=}Ta{=}O \end{array}$, in which the metal is still quinquivalent.

It is produced by exposing tantalic oxide to an intense heat in a crucible lined with charcoal. It is a hard dark-grey substance, which, when heated in the air, is converted into tantalic oxide.

Hydrochloric or *Sulphuric Acid*, added in excess to a solution of alkaline tantalate, forms a precipitate of tantalic acid, which redissolves in excess of the hydrochloric, but not of the sulphuric acid. *Potassium ferrocyanide*, added to a very slightly acidulated solution of an alkaline tantalate, forms a yellow precipitate; the *ferricyanide*, a white precipitate. *Infusion of galls* forms a light-yellow precipitate, soluble in alkalis. When tantalic chloride is dissolved in strong sulphuric acid, and then water and metallic *zinc* are added, a fine blue colour is produced, which does not turn brown, but soon disappears.

Tantalic oxide fused with microcosmic salt in either blow-pipe flame forms a clear, colourless glass, which does not turn red on addition of a ferrous salt. With borax it also forms a transparent glass, which may be rendered opaque by interrupted blowing, or *flaming*.

METALS OF THE PLATINUM GROUP.

Gold, Au.	Platinum, Pt.	Palladium, Pd.
	Iridium, Ir.	Rhodium, Rh.
	Osmium, Os.	Ruthenium, Ru.

THESE metals, or such of them as were best known, were formerly included, along with silver and mercury, in the class of "noble metals," or metals whose oxides are reduced by heat. Palladium, rhodium, and iridium, however, oxidise when heated moderately in air or oxygen, though by strong ignition their oxides are decomposed into oxygen and metal, while ruthenium and osmium unite with oxygen forming volatile oxides which are not completely decomposed even at high temperatures.

Platinum and the metals immediately associated with it may be naturally grouped into two subdivisions, in each of which there is a remarkable gradation of physical properties as well as of atomic weights. With one of these gold is closely connected, and with the other there are many reasons for associating silver, though the compounds of silver so evidently resemble cuprous compounds that it has been thought best to class that metal with copper.

The following tabular statement will exhibit clearly the general relations of these metals to one another, though their position in the periodic system has always been a question of difficulty.

Gold is undoubtedly triad; the platinum metals proper are usually regarded as tetrad.

	At. Wt.	Dens.		At. Wt.	Dens.
Au, . .	197	19·3	Ag, . .	108	10·5
Pt, . .	194·3	21·5	Pd, . .	106·2	11·5
Ir, . .	192·5	22·4	Ro, . .	102·7	12·0
Os, . .	190·3	22·48	Ru, . .	101·4	12·06

GOLD.

Symbol, Au (Aurum). Atomic weight, 197.

Gold, in small quantities, is a very widely diffused metal; traces of it are constantly found in the more ancient rocks. It is always met with in the metallic state, sometimes beautifully crystallised in the cubic form, associated with quartz, iron oxide, and other substances, in regular mineral veins. The sands and gravels which

result from the disintegration of such crystalline rocks, and which form the bed of many rivers, have long furnished gold derived from this source, the gold dust, in virtue of its high specific gravity, being easily separable by a simple process of washing. Formerly the chief supply of gold was obtained from the mines of Brazil, Hungary, and the Ural mountains; but California and Australia, South Africa and British Columbia, now yield by far the largest quantity.

Native gold is almost always alloyed with silver. The purest specimens have been obtained from Schabrowski, near Katharinenburg, in the Ural. A specimen analysed by Gustav Rose was found to contain 98·96 per cent. of gold. The Californian gold averages from 87·5 to 88·5 per cent., and the Australian from 96 to 96·6 per cent. In some specimens of native gold, as in that from Linarowski, in the Altai mountains, the percentage of gold is as low as 60 per cent., the remainder being silver.

When a veinstone is wrought for gold, it is stamped to powder and ground or shaken in a proper apparatus with water and mercury, which immediately dissolves the fine particles of metal, forming an amalgam from which the gold and the quicksilver can be recovered by distillation in an iron retort.

Poor ores containing only a minute proportion of gold can be treated with some chemical agent which takes the gold into aqueous solution. Auriferous pyrites, for example, is first roasted and then exposed in the presence of water to the action of chlorine or bromine under slight pressure. The gold is thus dissolved out in the form of chloride or bromide, from which the metal can afterwards be precipitated by ferrous sulphate. Potassium cyanide is now taking the place of chlorine for effecting solution of the gold which passes into solution as a double cyanide :

$$Au_2 + 4KCy + \underset{\text{from air.}}{O} + H_2O = 2KCy.AuCy + 2KHO$$

The precious metal is precipitated by metallic zinc or by some electrolytic process.

Gold is refined by the action of chlorine or of acids. If the proportion of silver present is small, the metal is melted and a stream of chlorine gas passed through it till the impurities have been converted into chlorides. More commonly the gold is melted with copper or silver, and in such proportion that the alloy does not contain more than about a quarter of its weight of gold. It is then boiled with strong sulphuric acid in cast-iron pots. This constitutes the operation known as *parting*. The copper and silver are converted into sulphates, whilst the residual gold is washed, dried, melted in crucibles, and cast into bars.

Pure gold is obtained from its alloys by solution in nitromuriatic acid, and precipitated with a ferrous salt, which reduces the gold and is converted into a ferric salt, thus :

$$6FeSO_4 + 2AuCl_3 = 2Fe_2(SO_4)_3 + Fe_2Cl_6 + Au_2.$$

The gold falls as a brown powder, which acquires the metallic lustre by friction.

Gold is a soft metal, having a beautiful yellow colour. It surpasses all other metals in malleability, the thinnest gold leaf not exceeding, it is said, $\frac{1}{200000}$ of an inch in thickness, while the gilding on the silver wire used in the manufacture of *gold-lace* is still thinner. It may also be drawn into very fine wire. Gold has the density 19·5 ; it melts at 1037°, a temperature above the fusing point of silver. Neither air nor water affects it in the least at any temperature ; the ordinary acids fail to attack it singly. A mixture of nitric and hydrochloric acid dissolves gold, however, with ease, the active agent being the liberated chlorine.

Gold intended for coin, and most other purposes, is always alloyed with a certain proportion of silver or copper, to increase its hardness and durability : the first-named metal confers a pale greenish colour. English standard gold contains $\frac{1}{12}$ of alloy, now always copper. Gold when alloyed with copper may be estimated by fusion in a cupel with lead, in the same way as silver (p. 440). If the alloy be free from silver, the weight of the globule of gold left in the cupel will, after repeated fusions, accurately represent the quantity of gold which is present in the alloy. But if the alloy contains silver, that metal remains with the gold after cupellation. In this case the original alloy, consisting of gold, silver, and copper, is fused in the muffle, together with lead and silver ; the alloy of gold and silver remaining after cupellation is then boiled with nitric acid, which dissolves the silver, the gold being left behind. By this treatment, however, an accurate separation of the two metals is obtained only when they are present in certain proportions. If the alloy contains but little silver, that metal is protected from the action of the nitric acid by the gold ; and if it contains too much silver, the gold is left as a powder when the silver is dissolved out. Experience has shown that the most favourable proportions are $\frac{1}{4}$ gold to $\frac{3}{4}$ silver ; the gold is then left pure, retaining the original shape of the alloy, and can be easily dried and weighed. The quantity of silver which is added to the alloy must therefore vary with the amount of gold which it contains.

Gold-leaf is made by rolling out plates of pure gold as thin as possible, and then beating them between folds of membrane with a heavy hammer, until the requisite degree of tenuity has been reached. The leaf is made to adhere to wood, etc., by size or varnish.

Gilding on copper is sometimes performed by dipping the articles into a solution of mercury nitrate, and then shaking them with a small lump of a soft amalgam of gold, which thus becomes spread over their surfaces : the articles are subsequently heated to expel the mercury, and then burnished. Gilding on steel may be effected either by applying a solution of auric chloride in ether, or by roughening the surface of the metal, heating it, and applying gold-leaf with the burnisher. Gilding is commonly effected by electrolysis as already described (p. 299). The solution usually employed is

obtained by dissolving chloride of gold in a solution of potassium cyanide.

Gold forms two series of compounds: the aurous compounds, in which it is apparently univalent, as $AuCl$, Au_2O, etc., and the auric compounds, in which it is trivalent, as $AuCl_3$, Au_2O_3, etc.

Chlorides.—*Aurous Chloride*, $AuCl$ or more probably Au_2Cl_2, is produced when the trichloride is evaporated to dryness, and exposed to a temperature of 227° until chlorine ceases to be evolved. It forms a yellowish-white mass, insoluble in water. In contact with that liquid it is decomposed slowly in the cold, and rapidly by the aid of heat, into metallic gold and trichloride.

Intermediate *Auroso-auric Chloride*, Au_2Cl_4, is a slightly volatile substance formed by the action of chlorine on finely-divided gold.

Auric Chloride, $AuCl_3$, is the most important compound of gold: it is always produced when gold is dissolved in nitro-muriatic acid. The deep yellow solution thus obtained yields, by evaporation, yellow crystals of the double chloride of gold and hydrogen, $HAuCl_4$; when this is cautiously heated, hydrochloric acid is expelled, and the residue, on cooling, solidifies to a red crystalline mass of auric chloride, very deliquescent, and soluble in water, alcohol, and ether. Auric chloride combines with a number of metallic chlorides, forming a series of double salts, called chloroaurates, of which the general formula in the anhydrous state is $MAuCl_4$ or $MCl,AuCl_3$, M representing an atom of a monad metal. These compounds are mostly yellow when in crystals, and red when deprived of water. The *ammonium salt*, $(NH_4)AuCl_4,H_2O$, crystallises in transparent needles; the sodium salt, $NaAuCl_4,2H_2O$, in long four-sided prisms. Auric chloride also forms crystalline double salts with the hydrochlorides of many organic bases.

A mixture of auric chloride with excess of acid potassium or sodium carbonate is used for gilding small ornamental articles of copper; these are cleaned by dilute nitric acid, and then boiled in the mixture for some time, by which means they acquire a thin but perfect coating of reduced gold.

Oxides.—*Aurous Oxide*, Au_2O, is produced when caustic potash is poured upon aurous chloride. It is a green powder, partly soluble in the alkaline liquid; the solution rapidly decomposes into metallic gold which subsides, and auric oxide which remains dissolved.

Auric Oxide, Au_2O_3.—When magnesia is added to auric chloride, and the sparingly soluble aurate of magnesium is well washed and digested with nitric acid, auric oxide is left as an insoluble reddish-yellow powder, which when dry becomes chestnut-brown. It is easily reduced by heat, and by mere exposure to light; it is insoluble in oxygen-acids, with the exception of strong nitric acid, insoluble in hydrofluoric acid, easily dissolved by hydrochloric and hydrobromic acids. Alkalis dissolve it freely; indeed its acid properties are very

strongly marked; it partially decomposes a solution of potassium chloride when boiled with that liquid, potassium hydroxide being produced. When digested with ammonia, it yields fulminating gold, consisting of $(AuN.NH_3)3H_2O$.

The compounds of auric oxide with alkalis are called aurates. The *potassium salt*, $K_2O,Au_2O_3,6H_2O$ or $KAuO_2,3H_2O$, is a crystalline salt, the solution of which is sometimes used as a bath for electro-gilding. A compound of aurate and acid sulphite of potassium, *potassium aurosulphite*, $2(KAuO_2,4KHSO_3),H_2O$, is deposited in yellow needles when potassium sulphite is added, drop by drop, to an alkaline solution of potassium aurate.

Gold shows but little tendency to form oxygen-salts. Auric oxide dissolves in strong nitric acid, but the solution is decomposed by evaporation or dilution. A *sodio-aurous thiosulphate*, $Na_3Au(S_2O_3)_2,2H_2O$, is prepared by mixing the concentrated solutions of auric chloride and sodium thiosulphate, and precipitating with alcohol. It is very soluble in water, and crystallises in colourless needles. With barium chloride, it yields a gelatinous precipitate of *bario-aurous thiosulphate*, $Ba_3Au_2(S_2O_3)_4$.

Sulphides.—*Aurous Sulphide*, Au_2S, is formed as a dark brown, almost black precipitate when hydrogen sulphide is passed into a boiling solution of auric chloride. It forms sulphur-salts, with the monosulphides of potassium and sodium. *Auric sulphide*, Au_2S_3, is precipitated in yellow flocks when hydrogen sulphide is passed into a cold dilute solution of auric chloride. Both these sulphides dissolve in ammonium sulphide.

Reactions of Gold Compounds.—The presence of gold in solution may be detected by the brown precipitate produced with *ferrous sulphate*, fusible before the blow-pipe to a bead of metallic gold; also by the brownish-purple precipitate, called "Purple of Cassius," formed when *stannous chloride* is added to dilute gold solutions. The composition of this precipitate is not exactly known, but after ignition it doubtless consists of a mixture of stannic oxide and metallic gold. It is used in enamel painting.

Oxalic acid slowly reduces gold to the metallic state: to ensure complete precipitation, the gold solution must be digested with it for twenty-four hours.

$$2AuCl_3 + 3H_2O + 3H_2C_2O_4 = Au_2 + 6HCl + 3H_2O + 6CO_2.$$

Gold is also precipitated by nitrous acid, by sulphurous acid (when warmed), and by many organic substances.

PLATINUM.

Symbol, Pt. Atomic weight, 194·3.

This metal was discovered in the sands of certain rivers in South America, and being at first mistaken for an ore of silver was called

platina (diminutive of Spanish *plata*, silver), in reference to its white colour. *Crude platinum*, a native alloy of platinum, palladium, rhodium, iridium, and a little iron, occurs in grains and rolled masses, sometimes of tolerably large dimensions, mixed with gravel and transported materials, on the slopes of the Ural Mountains in Russia, also in Brazil, Ceylon, and a few other places.

From this substance platinum is prepared by the following process:—The crude metal is acted upon as far as possible by *aqua regia* containing an excess of hydrochloric acid and slightly diluted with water, in order to dissolve as small a quantity of iridium as possible: to the deep yellowish-red and highly acid solution thus produced, sal-ammoniac is added, by which nearly the whole of the platinum is thrown down in the state of ammonium platinochloride. This substance, washed with a little cold water, dried, and heated to redness, leaves metallic platinum in the spongy state. This metal cannot be fused into a compact mass by ordinary furnace-heat, but the same object may be accomplished by taking advantage of its property of welding, like iron, at a high temperature. According to the process formerly employed, the spongy platinum was made into a thin uniform paste with water, introduced into a slightly conical mould of brass, and subjected to a graduated pressure, by which the water was squeezed out, and the mass at length rendered sufficiently solid to bear handling. It was then dried, very carefully heated to whiteness, and hammered, or subjected to powerful pressure. If this operation is properly conducted, the platinum will then be in a state to bear forging into a bar, which can afterwards be rolled into plates, or drawn into wire, at pleasure.

A method of refining platinum by fusion, devised by Deville and Debray, is now usually adopted. The apparatus is as follows:—The lower part of the furnace consists of a piece of lime, hollowed out in the centre to the depth of about a quarter of an inch; a small notch is filed at one side of this basin, through which, after fusion, the metal is poured out. A cover made of another piece of lime fits on the top of this basin; it is also hollowed to a small extent, and has a conical perforation at the top, into which is inserted the nozzle of an oxy-hydrogen blow-pipe. The whole arrangement is firmly bound with iron bands. To use the apparatus, the stop-cock supplying the hydrogen (or coal-gas) is opened, and the gas lighted at the notch in the crucible; the oxygen is then gradually supplied; and when the furnace is sufficiently hot, the spongy metal obtained by the process already described is introduced in small pieces through the orifice. By this arrangement as much as 50 pounds of platinum and more may be fused at once.

Platinum is a little whiter than iron: it is exceedingly malleable and ductile, both hot and cold, and is very difficult to fuse, melting only before the oxy-hydrogen blow-pipe. It is one of the heaviest substances known, its density being 21·5. Neither air, moisture, nor the ordinary acids attack platinum in the slightest degree at any temperature: hence its great value in the construction of chemical

apparatus. It is dissolved by *aqua regia*, and superficially oxidised by fused potassium hydroxide, which enters into combination with the oxide.

Capsules and crucibles of platinum are of great value to the chemist; the latter are constantly used in mineral analyses for fusing siliceous matter with alkaline carbonates. They suffer no injury in this operation, although caustic alkali roughens and corrodes the metal. The experimenter must be particularly careful to avoid introducing any oxide of an easily fusible metal, as that of lead or tin, into a platinum crucible. If reduction should by any means occur, these metals will at once alloy themselves with the platinum, and the vessel will be destroyed. Platinum is also attacked by many fusible sulphides, such as sulphide of antimony. A platinum crucible must never be put naked into a coke or charcoal fire, but always placed within a covered earthen crucible.

The remarkable property of the spongy metal to determine the union of oxygen and hydrogen has been already noticed (p. 67). *Platinum-black*, in which the division is carried much further, is prepared by boiling a solution of platinic chloride to which an excess of sodium carbonate and some sugar have been added, until the precipitate formed after a little time becomes perfectly black, and the supernatant liquid colourless. The black powder is collected on a filter, washed, and dried by gentle heat. This substance appears to possess the property of condensing gases, more especially oxygen, into its pores to a very great extent. When placed in a solution of formic acid, it converts the latter, with copious effervescence, into carbonic acid; alcohol, dropped upon the platinum-black, is oxidised to acetic acid, the rise of temperature being often sufficiently great to cause ignition. When exposed to a red heat, the black substance shrinks in volume and assumes the appearance of common spongy platinum.

Platinum forms two series of compounds: the platinous compounds, in which it is apparently bivalent, *e.g.*, $PtCl_2$, PtO, and the platinic compounds, in which it is quadrivalent, *e.g.*, $PtCl_4$, PtO_2, etc.

Few oxysalts of platinum are known, one of the most definite being a platinic pyrophosphate, PtP_2O_7, which is obtained as a yellow insoluble powder when platinum is heated with phosphoric anhydride in the presence of oxygen (Barnett).

Chlorides.—*Platinous Chloride*, $PtCl_2$ or Pt_2Cl_4, is produced when platinic chloride, dried and powdered, is exposed for some time to a temperature of about 200°, whereby half the chlorine is expelled; also, when sulphurous acid gas is passed into a solution of the tetrachloride until the latter ceases to give a precipitate with sal-ammoniac. It is a greenish-grey powder, insoluble in water, but dissolved by hydrochloric acid. The latter solution, mixed with sal-ammoniac or potassium chloride, deposits a double salt in fine red prismatic crystals, containing, in the last case, K_2PtCl_4 or

$2KCl,PtCl_2$. The corresponding sodium compound is very soluble, and difficult to crystallise. These double salts are called *platinoso-chlorides* or *chloroplatinites.* Platinous chloride is decomposed by heat into chlorine and metallic platinum.

Platinous chloride unites with carbon monoxide, forming the three compounds $PtCl_2CO$, $2PtCl_23CO$, and $PtCl_22CO$, all of which are produced by heating platinous chloride in a stream of carbon monoxide. The first and third crystallise in yellow needles, the second in white needles.

Platinous chloride also unites with phosphorus trichloride, forming the compounds $PtCl_2.PCl_3$ and $PtCl_2.2PCl_3$. These two chlorides are converted by water—the latter on exposure to moist air at a low winter temperature—into p h o s p h o p l a t i n i c and d i p h o s p h o-p l a t i n i c a c i d s, $Cl_2Pt—P(OH)_3$ and $Cl_2Pt\left\langle\begin{matrix}P(OH)_3\\ | \\ P(OH)_3\end{matrix}\right.$, the former of which is tribasic, the latter sexbasic.

Platinum Tetrachloride, or *Platinic Chloride*, $PtCl_4$, is always formed when platinum is dissolved in *aqua regia.* The acid solution yields, on evaporation, an orange-brown residue, deliquescent, and very soluble both in water and in alcohol; it contains the compound $2HCl.PCl_4$ or H_2PtCl_6, which may be called chloroplatinic acid. Platinic chloride unites with a great variety of metallic chlorides, forming double salts called *platino-chlorides* or *chloro-platinates*; the most important of these compounds are those containing the metals of the alkalis, and ammonium. *Potassium platinochloride*, $2KCl.PtCl_4$, or K_2PtCl_6, forms a bright-yellow crystalline precipitate, being produced whenever solutions of the chlorides of platinum and of potassium are mixed, or a potassium salt mixed with a little hydrochloric acid is added to platinum tetrachloride. It is feebly soluble in water, still less soluble in dilute alcohol, and is decomposed with some difficulty by heat. It is easily reduced by hydrogen at a high temperature, yielding a mixture of potassium chloride and platinum-black: the latter substance may thus, indeed, be very easily prepared. The *sodium salt*, $2NaCl.PtCl_4,6H_2O$, or $Na_2PtCl_6,6H_2O$, is very soluble, crystallising in large, transparent, yellow-red prisms. The *ammonium salt*, $2NH_4Cl.PtCl_4$, is indistinguishable, in physical characters, from the potassium salt; it is thrown down as a precipitate of small, transparent, yellow, octahedral crystals when sal-ammoniac is mixed with platinic chloride; it is but feebly soluble in water, still less so in dilute alcohol, and is decomposed by heat, yielding spongy platinum, while sal-ammoniac, hydrochloric acid, and nitrogen are driven off. Platinic chloride also forms crystallisable double salts with the hydrochlorides of many organic bases; with ethylamine, for example, the compound,

$$2[NH_2(C_2H_5),HCl]PtCl_4 \text{ or } [NH_3(C_2H_5)]_2PtCl_6.$$

The *bromides* and *iodides of platinum* are analogous in composition

to the *chlorides*, and likewise form double salts with alkaline bromides and iodides.

Experiments.—1. Dissolve a piece of platinum foil in *aqua regia* (3 vols. hydrochloric with 1 vol. nitric acid) in a flask. Pour the solution into a dish, and evaporate on the water-bath to dryness.

2. Redissolve the residue in a small quantity of water, and add an excess of solution of ammonium chloride. Stir the mixture with a glass rod, and after a few minutes filter off the precipitate from the nearly colourless solution. Drain the precipitate, dry it, and heat it, at first gently, in a covered porcelain crucible, till the chloride is completely decomposed. Try some of the experiments described (p. 68).

Oxides.—*Platinous Oxide*, PtO or Pt_2O_2, is obtained by digesting the dichloride with caustic potash, as a black powder, soluble in excess of alkali. It dissolves also in acids with brown colour, and the solutions are not precipitated by sal-ammoniac. When platinum dioxide is heated with solution of oxalic acid, it is reduced to monoxide, which remains dissolved. The liquid has a dark-blue colour, and deposits fine copper-red needles of platinous oxalate.

The *Dioxide*, or *Platinic Oxide*, PtO_2, is best prepared by boiling platinic chloride with a great excess of caustic soda, and then adding acetic acid. The precipitate, dried at 100°, yields a brown powder, PtH_4O_4, which at a higher temperature becomes black and anhydrous. It dissolves in acids, and combines with alkalis: the salts have a yellow or red tint, and a great disposition to unite with salts of the alkalis and alkaline earths, giving rise to a series of double compounds, which are not precipitated by excess of alkali. Both oxides of platinum are reduced to the metallic state by ignition.

Sulphides.—The compounds PtS and PtS_2, are produced by the action of hydrogen sulphide, or the hydrosulphide of an alkali-metal, on the dichloride and tetrachloride of platinum respectively; they are both black substances, insoluble in water. Platinic sulphide heated in a close vessel gives off half its sulphur, and is reduced to platinous sulphide. It dissolves in alkaline hydroxides, carbonates, and sulphides, forming salts called *thioplatinates*, which are decomposed by acids.

Ammoniacal Platinum Compounds.—The chlorides, oxides, sulphates, etc., of platinum are capable of taking up two or more molecules of ammonia, and forming compounds analogous in many respects to the ammoniacal mercury compounds already described.

The platinum in some of these compounds is bivalent (*platoso*), and unites by two of its combining units with the bivalent groups, NH_3 or N_2H_6, each of which retains one combining unit free. In others the platinum is quadrivalent (*platino*), and unites by some of its combining units with ammonia or diammonia, the remaining units being satisfied by combination with electro-negative radicles.

In others, again, the platinum accumulates in such a manner as to form compounds containing $(Pt_2)''$, $(Pt^{iv}—Pt^{iv})^{vi}$, $(Pt^{iv}—Pt^{iv}—Pt^{iv}—Pt^{iv})^{x}$, etc. The bivalent groups, NH_3, N_2H_6, always go by pairs, excepting in the semi-diammoniums, in which half or a quarter of the combining units of the platinum is satisfied by once N_2H_6.

The names and constitution of the several groups are given in the following table, the symbol R denoting a univalent chlorous radicle, such as Cl, NO_2, etc.

1. Platosammonium compounds,	$Pt<\begin{matrix}NH_3R\\NH_3R\end{matrix}$
2. Platosemidiammonium compounds,	$Pt<\begin{matrix}NH_2(NH_4)R\\R\end{matrix}$
3. Platomonodiammonium compounds,	$Pt<\begin{matrix}NH_2(NH_4)R\\NH_3R\end{matrix}$
4. Platosodiammonium compounds,	$Pt<\begin{matrix}NH_2(NH_4)R\\NH_2(NH_4)R\end{matrix}$
5. Platinammonium compounds,	$R_2Pt<\begin{matrix}NH_3R\\NH_3R\end{matrix}$
6. Platinosemidiammonium compounds,	$R_2Pt<\begin{matrix}NH_2(NH_4)R\\R\end{matrix}$
7. Platinomonodiammonium compounds,	$R_2Pt<\begin{matrix}NH_2(NH_4)R\\NH_3R\end{matrix}$
8. Platinodiammonium compounds,	$R_2Pt<\begin{matrix}NH_2(NH_4)R\\NH_2(NH_4)R\end{matrix}$
9. Diplatinammonium compounds,	$\begin{matrix}RPt<\begin{matrix}NH_3R\\NH_3R\end{matrix}\\ \vert \\ RPt<\begin{matrix}NH_3R\\NH_3R\end{matrix}\end{matrix}$
10. Diplatosodiammonium compounds,	$\begin{matrix}Pt—NH_2(NH_4)R\\ \vert \\ Pt—NH_2(NH_4)R\end{matrix}$
11. Diplatinodiammonium compounds,	$\begin{matrix}R_2Pt—NH_2(NH_4)R\\ \vert \\ R_2Pt—NH_2(NH_4)R\end{matrix}$
12. Diplatinotetradiammonium compounds,	$\begin{matrix}RPt<\begin{matrix}NH_2(NH_4)R\\NH_2(NH_4)R\end{matrix}\\ \vert \\ RPt<\begin{matrix}NH_2(NH_4)R\\NH_2(NH_4)R\end{matrix}\end{matrix}$

We shall here describe the most characteristic compounds of each group, referring for more complete description to larger works.

1. *Platosammonium Compounds.*—These compounds are formed by abstraction of the elements of ammonia, NH_3, from the

corresponding platosodiammonium-compounds. They are for the most part insoluble in water, but dissolve in ammonia, reproducing the platosodiammonium-compounds. They detonate when heated.

The *Chloride*, $Pt{<}^{NH_3Cl}_{NH_3Cl}$ or $N_2H_6PtCl_2$, is formed by heating platosodiammonium chloride to 220–270°, or by heating the same salt with hydrochloric acid, or by boiling the green salt of Magnus (p. 556) with nitrate or sulphate of ammonium, and is deposited as a yellow crystalline powder, or in rhombohedral scales. It dissolves in 4472 parts of water at 0° and in 130 parts of boiling water. At 270° it decomposes in the manner represented by the equation,

$$3N_2H_6PtCl_2 = 3Pt + 4NH_4Cl + 2HCl + N_2.$$

Silver nitrate added to its solution throws down all the chlorine. This salt is isomeric with the green salt of Magnus, with the yellow chloride of platosemidiammonium, and with the chloroplatinite of platosomonodiammonium.

The corresponding *iodide*, $N_2H_6PtI_2$, is a yellow powder, obtained by heating the aqueous solution of the compound $N_4H_{12}PtI_2$. It dissolves in ammonia, reproducing the latter compound. The *oxide*, N_2H_6PtO, obtained by heating platosodiammonium oxide (p. 556) to 110°, is a greyish mass, which when heated to 100° in a close vessel, gives off water, ammonia, and nitrogen, and leaves metallic platinum. The *hydroxide*, $N_2H_6Pt(HO)_2$, obtained by decomposing the sulphate with baryta-water, is a strong base, soluble in water, having an alkaline reaction, absorbing carbonic acid from the air, and liberating ammonia from its salts (Odling). The *sulphate*, $N_2H_6PtSO_4,H_2O$, and the *nitrate*, $N_2H_6Pt(NO_3)_2$, are obtained by boiling the iodide with sulphate and nitrate of silver: they are crystalline, and have a strong acid reaction. The sulphate retains a molecule of crystallisation-water, which cannot be removed without decomposing the salt.

2. *Platososemidiammonium Compounds.*—These compounds, isomeric with the preceding, are formed by direct addition of ammonia to platinous salts. The *chloride*, $Pt{<}^{N_2H_6Cl}_{Cl}$, is obtained by adding ammonia to a cold solution of platinous chloride in hydrochloric acid, filtering after 24 hours, and treating the yellowish-green residue with boiling water, which dissolves the platosemidiammonium salt, and leaves the green salt of Magnus formed at the same time. The solution on cooling deposits the platososemidiammonium chloride in small prisms, differing in form from the chloride above described, and much more soluble in water, requiring for solution 387 parts of cold and 26 parts of boiling water. The other salts of this base are obtained by decomposing the chloride with the corresponding silver salts. The *bromide* and *iodide* crystallise in yellow needles; the *nitrite* in silky needles, which detonate

when heated; the *nitrate* and *sulphate* form yellowish crystalline crusts.

3. *Platosomonodiammonium Compounds*, $Pt<^{N_2H_6R}_{NH_3R}$.—The *chloroplatinite* of this series, $2N_3H_9PtCl_2,PtCl_2$, formed in small quantity on adding ammonia to a solution of platinous chloride, crystallises in brown square laminæ slightly soluble in cold, more soluble in boiling water. Treated with silver nitrate it is converted into platosomonodiammonium *nitrate*, and this, when heated with hydrochloric acid, yields the corresponding *chloride*, $N_3H_9PtCl_2$, which is very soluble, and crystallises in colourless needles or nacreous scales.

4. *Platosodiammonium Compounds*, $Pt<^{N_2H_6R}_{N_2H_6R}$.—The *chloride*, $N_4H_{12}PtCl_2$, one of the earliest discovered of the ammoniacal platinum compounds, is obtained by the action of ammonia on the green salt of Magnus, or on the chloride of platosammonium. When platinous chloride is boiled with excess of ammonia till the green precipitate formed in the first instance is redissolved, a solution is obtained, which, when filtered and evaporated, yields the chloride of platosodiammonium in splendid yellow crystals containing one molecule of water, which they give off at 110°. It is soluble in water, and its solution mixed with platinous chloride yields *platosodiammonium chloroplatinite*, $N_4H_{12}PtCl_2,PtCl_2$, isomeric with platosammonium chloride, and constituting the *green salt of Magnus*, the first discovered of the ammonia-platinum compounds. This last salt may also be prepared by passing sulphurous acid gas into a boiling solution of platinic chloride till it is completely converted into platinous chloride (and is therefore no longer precipitated by sal-ammoniac), and neutralising the solution with ammonia. It forms dark-green needles, insoluble in water, alcohol, and hydrochloric acid.

The *bromide* and *iodide* of this series are obtained by treating the solution of the sulphate with bromide or iodide of barium: they crystallise in cubes. The *oxide*, $N_4H_{12}PtO$, is obtained as a crystalline mass by decomposing the solution of the sulphate with an equivalent quantity of baryta-water, and evaporating the filtrate in a vacuum. It is strongly alkaline and caustic, like potash, absorbs carbonic acid rapidly from the air, and precipitates silver oxide from the solution of the nitrate. It is a strong base, neutralising acids completely, and expelling ammonia from its salts. It melts at 110°, giving off water and ammonia, and leaving platosammonium oxide. Its aqueous solution does not give off ammonia, even when boiled. The oxide absorbs carbon dioxide rapidly from the air, forming first a normal carbonate, $N_4H_{12}PtCO_3,H_2O$, and afterwards an acid salt, $N_4H_{12}PtCO_3,H_2CO_3$. The *sulphate*, $N_4H_{12}PtSO_4$, and the *nitrate*, $N_4H_{12}Pt(NO_3)_2$, are obtained by decomposing the chloride with silver sulphate or nitrate; they are neutral, and crystallise easily.

5. *Platinammonium Compounds.*—The chloride, $Cl_2Pt<^{NH_3Cl}_{NH_3Cl}$, is obtained by the action of chlorine on platosammonium chloride suspended in boiling water. It is a lemon-yellow crystalline powder, made up of quadratic octahedrons with truncated summits. It is insoluble in cold water, very slightly soluble in boiling water, or in water containing hydrochloric acid. It dissolves in boiling solution of ammonia, and the solution, on cooling, deposits a yellow precipitate, consisting of platinodiammonium chloride. It dissolves in boiling potash without evolving ammonia.

Nitrates.—An *oxynitrate*, $N_2H_6Pt(NO_3)_2O$, is obtained by boiling the chloride, $N_2H_6PtCl_4$, for several hours with dilute silver nitrate. It is a yellow crystalline powder, sparingly soluble in cold, more soluble in boiling water. The *normal nitrate*, $N_2H_6Pt(NO_3)_4$, is obtained by dissolving the oxynitrate in nitric acid : it is yellowish, insoluble in cold water, soluble in hot nitric acid.

The *oxide*, $N_2H_6PtO_2$, is obtained by adding ammonia to a boiling solution of platinammonium nitrate ; it is then precipitated in the form of a heavy, yellowish, crystalline powder, composed of small shining rhomboïdal prisms ; it is nearly insoluble in boiling water, and resists the action of boiling potash. Heated in a close vessel, it gives off water and ammonia, and leaves metallic platinum. It dissolves readily in dilute acids, even in acetic acid, and forms a large number of crystallisable salts, both neutral and acid, having a yellow colour, and sparingly soluble in water. Another compound of platinic oxide with ammonia, called *fulminating platinum*, whose composition has not been exactly ascertained, is produced by decomposing ammonium platino-chloride with aqueous potash. It is a straw-coloured powder, which detonates slightly when suddenly heated, but strongly when exposed to a gradually increasing heat.

6. *Platinosemidiammonium Compounds.* — Isomeric with the preceding. The *chloride*, $Cl_2Pt<^{N_2H_6Cl}_{Cl}$, formed by the action of chlorine on platinososemidiammonium chloride, crystallises in yellow six-sided plates belonging to the rhombic system, turning green at 100°, and dissolving in potash without evolution of ammonia. A *hydroxy-nitrate*, $(OH)_2Pt<^{N_2H_6.NO_3}_{OH}$, is obtained as an amorphous yellow precipitate by treating the chloride with silver nitrate. A *chloronitrate*, $Cl_2Pt<^{N_2H_6.NO_3}_{NO_3}$, obtained by the action of chlorine on platososemidiammonium nitrate, crystallises in small yellow needles.

7. *Platinomonodiammonium Compounds.*—The *chloride*, $Cl_2Pt<^{N_2H_6Cl}_{NH_3Cl}$, formed by the action of nitro-muriatic acid on plato-

somonodiammonium chloride, crystallises in rhombic or hexagonal plates. A *bromonitrate*, $Br_2Pt{<}^{N_2H_6(NO_3)}_{NH_3(NO_3)} + H_2O$, obtained by adding bromine to the nitrate of platosomonodiammonium, forms yellow soluble crusts.

8. *Platinodiammonium Compounds.* — The chloride, $PtCl_2{<}^{N_2H_6Cl}_{N_2H_6Cl}$, is obtained by passing chlorine gas into a solution of platosodiammonium chloride; by dissolving platinammonium chloride in ammonia, and expelling the excess of ammonia by evaporation; or by precipitating a solution of platinodiammonium oxynitrate, or chloronitrate, with hydrochloric acid. It is white, and dissolves in small quantity in boiling water, from which solution it is deposited in the form of transparent regular octahedrons, having a faint-yellow tint. When a solution of this salt is treated with silver nitrate, one-half of the chlorine is very easily precipitated, but to remove even a small portion of the remainder requires a long-continued action of the silver-salt. The *chlorobromide*, ${}^{Br}_{Cl}{>}Pt{<}^{N_2H_6Br}_{N_2H_6Cl}$, is obtained as a yellow precipitate by treating platinodiammonium chloride with bromine. A *basic nitrate*, ${}^{HO}_{NO_3}{>}Pt{<}^{N_2H_6.NO_3}_{N_2H_6.NO_3}$, is obtained by the action of nitric acid on platosodiammonium nitrate, as a white crystalline powder, converted by ammonia into the salt $(HO)_2Pt(N_2H_6.NO_3)_2$. The *chlorosulphate*, $Cl_2Pt{<}^{N_2H_6}_{H_2H_6}{>}SO_4$, formed by the action of sulphuric acid on the chloride, crystallises in slender transparent needles. A *chloroxalate*, $Cl_2Pt(N_2H_6)_2C_2O_4$, obtained by treating the chloride with ammonium oxalate, is a very soluble crystalline powder.

9. *Diplatinammonium Iodide*, $\begin{matrix} IPt(NH_3I)_2 \\ | \\ IPt(NH_3I)_2 \end{matrix}$, or $I_2(Pt_2)^{vi}(NH_3I)_4$, the only term of this series at present known, is obtained by treating platosammonium iodide with boiling potash, and the resulting yellow powder with hydriodic acid. It is a black amorphous substance, which when again treated with potash and hydriodic acid, yields the compound $I_2(Pt_4)^x(NH_3I)_8$, and this by similar treatment may be converted into the still more condensed compound $I_2(Pt_8)^{xviii}(NH_3I)_{16}$.

10. *Diplatosodiammonium Compounds.*—The *hydroxide*, $\begin{matrix} Pt—N_2H_6—OH \\ | \\ Pt—N_2H_6—OH \end{matrix}$, formed by the action of caustic soda on the chloride of platososemidiammonium, is a greyish crystalline insoluble powder, which detonates violently when heated. Treated

with hydrochloric acid, it yields a yellow powder, which is converted by boiling water into the *chloride*, $Pt_2(N_2H_6Cl)_2$.

11. *Diplatinodiammonium Chloride*, $\begin{array}{l} Cl_2Pt{-}NH_2(NH_4)Cl \\ \quad | \\ Cl_2Pt{-}NH_2(NH_4)Cl \end{array}$, is a yellow amorphous powder formed by the action of nitro-muriatic acid on the hydroxide of the preceding series.

12. *Diplatino-tetradiammonium Compounds*, $\begin{array}{l} RPt(N_2H_6R)_2 \\ | \\ RPt(N_2H_6R)_2 \end{array}$ or $N_8H_{24}Pt_2R_6$. An *oxynitrate*, $O\left\langle \begin{array}{l} Pt(N_2H_6.NO_3)_2 \\ | \\ Pt(N_2H_6.NO_3)_2 \end{array}\right.$ or $N_8H_{24}Pt_2(NO_3)_4O$, is produced by boiling platosodiammonium nitrate with nitric acid. It is a colourless, crystalline, detonating salt, slightly soluble in cold water, more soluble in boiling water, insoluble in nitric acid (Gerhardt). A *chloroxynitrate*, $N_8H_{24}Pt_2(NO_3)_4OCl_2$, discovered by Raewsky, is formed when Magnus's green salt is boiled with a large excess of nitric acid. Red fumes are then evolved, and the resulting solution deposits the chloroxynitrate in small brilliant needles, which deflagrate when heated, giving off water and sal-ammoniac, and leaving metallic platinum. The nitrate group in this salt may be replaced by an equivalent quantity of carbonic or oxalic radicle, yielding the compounds, $N_8H_{24}Pt_2(CO_3)_2OCl_2$, and $N_8H_{24}Pt_2(C_2O_4)_2OCl_2$, both of which are crystallisable, and sparingly soluble. A *basic oxalonitrate*, $N_8H_{24}Pt_2(C_2O_4)_2(NO_3)_2O$, insoluble in water, is obtained by adding ammonium oxalate to the oxynitrate.

Reactions of Platinum Salts.—Platinic chloride, or a platinic oxygen-salt, may be recognised in solution by the yellow precipitate which it forms with *sal-ammoniac*, decomposible by heat, with production of spongy metal.

Hydrogen sulphide and *ammonium sulphide* gradually form a brown precipitate of platinic sulphide, soluble in excess of ammonium sulphide. *Zinc* precipitates metallic platinum.

Platinic chloride and sodium platinochloride are employed in analysis to detect the presence of potassium and separate it from sodium. For the latter purpose, the alkaline salts are converted into chlorides, and mixed with an excess of platinic chloride in solution. The solution is then evaporated to dryness on a water bath, and the residue washed with alcohol, which dissolves the double sodium salt, but not the corresponding potassium compound, K_2PtCl_6.

IRIDIUM.

Symbol, Ir. Atomic weight, 193.

When crude platinum is dissolved into nitro-muriatic acid, a small quantity of a grey scaly metallic substance usually remains behind,

having altogether resisted the action of the acid: this is a native alloy of iridium and osmium, called *osmiridium* or *iridosmine*; it is reduced to powder, mixed with an equal weight of dry sodium chloride, and heated to redness in a glass tube, through which a stream of moist chlorine gas is transmitted. The further extremity of the tube is connected with a receiver containing solution of ammonia. The gas, under these circumstances, is rapidly absorbed, iridium chloride and osmium chloride being produced: the former remains in combination with the sodium chloride; the latter, being a volatile substance, is carried forward into the receiver, where it is decomposed by the water into osmic and hydrochloric acids, which combine with the alkali. The contents of the tube when cold are treated with water, by which the iridium and sodium chloride is dissolved out; this is mixed with an excess of sodium carbonate, and evaporated to dryness. The residue is ignited in a crucible, boiled with water, and dried; it then consists of a mixture of ferric oxide and a combination of iridium oxide with soda; it is reduced by hydrogen at a high temperature, and treated successively with water and strong hydrochloric acid, by which the alkali and the iron are removed, while metallic iridium is left in a finely divided state. By strong pressure and exposure to a white heat, a certain degree of compactness may be communicated to the metal.

Iridium is a white brittle metal, fusible with great difficulty before the oxy-hydrogen blow-pipe. Deville and Debray, by means of their powerful oxy-hydrogen blast-furnace, fused it completely into a pure white mass, resembling polished steel, brittle in the cold, somewhat malleable at a red heat, and having a density equal to that of platinum, viz., 22·4. By moistening the pulverulent metal with a small quantity of water, pressing it tightly, first between filtering paper, then very forcibly in a press, and calcining it at a white heat in a forge fire, it may be obtained in the form of a compact, very hard mass, capable of taking a good polish, but still very porous, and of a density not exceeding 16·0. After strong ignition it is insoluble in all acids, but when reduced by hydrogen at low temperatures, it oxidises slowly at a red heat, and dissolves in nitro-muriatic acid. It is usually rendered soluble by fusing it with nitre and caustic potash, or by mixing it with common salt, or better, with a mixture of the chlorides of potassium and sodium, and igniting it in a current of chlorine, as above described.

Iridium forms three series of compounds, namely, the hypo-iridious compounds, as $IrCl_2$ or Ir_2Cl_4; the iridious compounds, *e.g.*, $IrCl_3$ or Ir_2Cl_6; and the iridic compounds, in which it is quadrivalent, as in $IrCl_4$, IrO_2, etc. It forms also a trioxide, IrO_3, in which it appears to be sexvalent.

Chlorides.—The *Dichloride*, $IrCl_2$ or Ir_2Cl_4, is a dark coloured mass, and appears to exist in certain double salts, called *hypo-chloriridites.*

The *Trichloride*, or *Iridious Chloride*, $IrCl_3$ or Ir_2Cl_6, is prepared by

strongly heating iridium with nitre, adding water and enough nitric acid to saturate the alkali, warming the mixture, and then dissolving the precipitated hydrate of the sesquioxide in hydrochloric acid ; it forms a dark yellowish-brown solution. This substance combines with other metallic chlorides, forming compounds called *iridoso-chlorides*, or *chloriridites*, which may be prepared by reducing the corresponding chloriridiates with sulphurous acid, hydrogen sulphide, or potassium ferrocyanide. Claus has obtained the compounds $IrCl_3,3NH_4Cl,3H_2O$, $IrCl_3,3KCl,3H_2O$, and $IrCl_3,3NaCl,12H_2O$. They are olive-green pulverulent salts, soluble in water.

The *Tetrachloride*, or *Iridic Chloride*, $IrCl_4$, is obtained in solution by dissolving very finely divided iridium, or one of its oxides, or the trichloride, in nitro-muriatic acid, and heating the liquid to the boiling-point. On evaporating the solution, it remains in the form of a black, deliquescent, amorphous mass, translucent with dark-red colour at the edges ; soluble, with reddish-yellow colour, in water. It unites with alkaline chlorides, forming compounds called *iridio-chlorides*, or *chloriridiates*, analogous in composition to the chloroplatinates. The *ammonium salt*, $(NH_4)_2IrCl_6,H_2O$, and the *potassium salt*, K_2IrCl_6, or $2KCl,IrCl_4$, are formed, as dark-brown crystalline precipitates, on mixing the solutions of the component chlorides. The potassium salt may also be prepared by passing chlorine over a gently ignited and finely divided mixture of iridium with potassium chloride. It is soluble in boiling water, and crystallises in black octahedrons, yielding a red powder. The *sodium salt*, $Na_2IrCl_6,6H_2O$, prepared like the potassium salt, forms easily soluble black tables and prisms, isomorphous with the corresponding platinum salt.

Oxides.—Iridium forms four oxides, IrO, Ir_2O_3, IrO_2, and IrO_3, *Hypoiridious Oxide*, IrO, is but little known. On exposure to the air it is quickly converted into a higher oxide.

The *Sesquioxide* or *Iridious Oxide*, Ir_2O_3, was formerly regarded as the most easily formed and most stable of the oxides of iridium ; but, according to Claus, it has a great tendency to take up oxygen and pass to the state of dioxide. It may be prepared by gently igniting a mixture of potassium chloriridite $(K_6Ir_2Cl_3)$ with sodium carbonate in an atmosphere of carbon dioxide ; on treating the product with water, the sesquioxide remains in the form of a black powder insoluble in acids. The *Trihydroxide* or *Iridious Hydroxide*, $Ir_2(OH)_6$, is prepared like the corresponding rhodium compound, which it closely resembles.

Iridious oxide unites with basic oxides, forming salts which may be called *iridites*. A solution of a chloriridite in excess of lime-water deposits, after standing for some time out of contact of air, a dirty yellow precipitate containing $3CaO,Ir_2O_3$.

Iridic Oxide, IrO_2, is a black powder obtained by heating the tetrahydroxide in a current of carbon dioxide. It is insoluble in acids.—The *Tetrahydroxide*, or *Iridic Hydroxide*, $Ir(OH)_4$, formed by

oxidation of iridious hydroxide in the air, or by precipitating the tetrachloride with an alkali, is a heavy indigo-blue powder, almost insoluble in dilute sulphuric and nitric acids, but dissolving slowly in hydrochloric acid. The indigo-blue solution when heated turns green, and afterwards brown.

Iridic Peroxide, IO_3, is obtained as a potassium salt by fusing the metal with nitre.

Iridium, like the other platinum metals, shows but little tendency to form oxygen salts. The oxides dissolve in acids, but no definite salts are obtained in this way. The solution of iridic oxide in sulphuric acid has a dark-brown colour, which is not modified by potash in the same manner as that of the dichloride; neither does it yield any blue precipitate on boiling.

The only definite oxygen-salts of iridium that have been obtained are an iridious sulphate and double salts derived from sulphurous and dithionic acids.

Iridious Sulphite, $Ir_2(SO_3)_3,6H_2O$, is formed by passing sulphur dioxide into water, holding the trioxide in suspension, and separates from solution on evaporation as a yellow crystalline precipitate.

Hypo-iridoso-potassic Sulphite, $K_6Ir_2(SO_3)_4$, is obtained as a white crystalline powder, when the mother-liquor obtained in preparing potassium chloriridite by passing sulphurous oxide through a solution of the chloriridate, is evaporated to a small bulk.

Ammoniacal Compounds of Iridium.—The *Chlorides of Iridosammonium* and *Iridosodiammonium*, $Ir(NH_3Cl)_2$, and $Ir[NH_2(NH_4)Cl]_2$, together with the corresponding sulphates, are prepared like the platinous compounds of analogous composition, which they also resemble in their properties. The *chloronitrate*, $Ir{<}^{NH_2(NH_4)NO_3}_{NH_2(NH_4)Cl}$, is formed by heating the chloride, $Ir(NH_2Cl)_2$, with strong nitric acid. *Iridiodiammonium chloride*, $Cl_2Ir[NH_2(NH_4)Cl]_2$, is obtained as a violet precipitate by treating the nitrate just mentioned with hydrochloric acid.

The compound $10NH_3,Ir_2Cl_6$, analogous to the rhodium-compound described on p. 570, but having no analogue in the platinum series, is obtained as a flesh-coloured crystalline powder by prolonged digestion of ammonium chloriridate with warm aqueous ammonia. The corresponding carbonate, nitrate, and sulphate have also been prepared.

Iridic solutions (containing the dioxide or tetrachloride) are of a dark brown-red colour; iridious solutions (containing the sesquioxide or trichloride) have an olive-green colour. The characters of an iridic solution are best observed with sodium chloriridate, all the other iridic compounds being but slightly soluble.

Iridic solutions give with *ammonium* or *potassium chloride* a crystalline precipitate of ammonium or potassium chloriridate, which

is distinguished from the corresponding platinum precipitate by its dark brown-red colour, and further by its reduction to soluble chlor-iridite when treated with solution of hydrogen sulphide. This reaction serves for the separation of iridium from platinum.

OSMIUM.

Symbol, Os. Atomic weight, 190·3.

The separation of this metal from iridium, ruthenium, and the other metals with which it is associated in native osmiridium, and in platinum residues, depends chiefly on its ready oxidation with nitric or nitro-muriatic acid, or by ignition in air or oxygen, and the volatility of the oxide thus produced.

To prepare metallic osmium, the alkaline solution of osmic acid obtained in the preparation of iridium or of ruthenium is mixed with excess of hydrochloric acid, and digested with mercury at 40°. The osmium is then reduced by the mercury, and an amalgam is formed, which, when distilled in a stream of hydrogen till all the mercury and calomel are expelled, leaves metallic osmium in the form of a black powder. The metal may also be obtained by igniting ammonium chloro-osmite with sal-ammoniac. Deville and Debray prepared it by passing the vapour of the pure tetroxide mixed with carbon monoxide and carbon dioxide through a red-hot porcelain tube.

The properties of osmium vary according to its mode of preparation. In the pulverulent state it is black, destitute of metallic lustre, which, however, it acquires by burnishing. It may also be rendered crystalline by fusing with three or four parts of tin in a charcoal-lined crucible, treating the crystalline alloy with hydrochloric acid to remove the tin, and heating the residue in a current of hydrochloric acid gas. The crystals are cubes or very obtuse rhombohedrons, having a bluish-white colour with violet lustre; they are harder than glass, and have the density 22·477, which is higher than that of any other known substance. At a very high temperature, capable of melting ruthenium and iridium and volatilising platinum, osmium likewise volatilises, but still does not melt; in fact it is the most refractory of all metals.

Osmium in the finely-divided state is highly combustible, continuing to burn when set on fire, till it is all volatilised as tetroxide. In this state also it is easily oxidised by nitric or nitro-muriatic acid, being converted into tetroxide. But after exposure to a red heat it becomes less combustible, and is not oxidised by nitric or nitro-muriatic acid.

Osmium Chlorides.—Osmium forms three chlorides, analogous to those of iridium and ruthenium. When it is heated in dry chlorine gas, there is formed, first a blue-black sublimate of the dichloride, then a red sublimate of the tetrachloride. The *dichloride*,

or *hypo-osmious chloride*, $OsCl_2$ or Os_2Cl_4, dissolves in water with dark violet-blue colour. It is likewise formed by the action of reducing agents on either of the higher chlorides, into which, on the other hand, it is easily converted by oxidation. The addition of potassium chloride renders it more stable, by forming a double salt. The *trichloride* has not been isolated, but is contained in the solution obtained by treating the sesquioxide with hydrochloric acid. It forms double salts with alkaline chlorides. The *potassium salt*, $K_6Os_2Cl_{12},6H_2O$, is produced, together with potassium chlorosmate, when a mixture of pulverised osmium and potassium chloride is ignited in chlorine gas; it forms dark red-brown crystals.

The *Tetrachloride*, or *Osmic Chloride*, $OsCl_4$, is the red compound which constitutes the principal part of the product obtained by igniting osmium in chlorine gas.

Osmic chloride unites with the chlorides of the alkali-metals. forming salts sometimes called osmiochlorides, or chlorosmates.

Sodium Osmiochloride, Na_2OsCl_6, prepared by heating a mixture of osmium sulphide and sodium chloride in a current of chlorine, crystallises in orange-coloured rhombic prisms, an inch long, easily soluble in water and in alcohol. The *potassium* and *ammonium salts*, of analogous composition, are obtained as red-brown crystalline precipitates on adding sal-ammoniac or potassium chloride to the solution of the sodium salt.

Oxides.—Osmium forms five oxides analogous to those of ruthenium. *Hypo-osmious Oxide*, OsO, is obtained by igniting hypo-osmious sulphite in a stream of carbonic acid gas; also as a blue-black hydrate, by heating the same salt with strong potash solution in a closed vessel. *Hypo-osmious Sulphite*, $OsSO_3$, is a black-blue salt, produced by mixing the aqueous solution of osmium tetroxide with sulphurous acid.—The *Sesquioxide*, or *Osmious Oxide*, Os_2O_3, is obtained by heating either of the double salts of the trichloride with sodium carbonate in a stream of carbonic acid gas It is a black powder, insoluble in acids. The *hydroxide*, obtained by precipitation, has a dirty brown-red colour, is soluble in acids, but does not yield pure salts.

The *Dioxide*, or *Osmious Oxide*, OsO_2, is obtained as a black insoluble powder, by heating potassium osmiochloride with sodium carbonate in a stream of carbonic acid gas, or in copper-red metallic shining lumps, by heating the corresponding hydroxide. *Osmious Hydroxide*, or *Osmious Acid*, $Os(OH)_4$, is obtained by precipitating a solution of potassium osmio-chloride with boiling potash, or in greater purity by mixing a solution of potassium osmate, K_2OsO_4, with dilute nitric acid according to the equation,

$$2K_2OsO_4 + 4HNO_3 = Os(OH)_4 + OsO_4 + 4KNO_3.$$

The *Trioxide*, OsO_3, and the corresponding hydroxide or *Osmic Acid*, H_2OsO_4, ar not known, but the osmates of alkali-

metals are formed by the action of reducing agents in presence of alkalis on the tetroxide. The *potassium salt*, $K_2OsO_4,2H_2O$, is a rose-coloured crystalline powder.

The *Tetroxide*, OsO_4, often called *Perosmic Acid*, is the volatile strong-smelling compound, formed when osmium or either of its lower oxides is heated in the air or treated with nitric or nitro-hydrochloric acid. It may be prepared by heating osmium in a current of oxygen gas, and condenses in the cool part of the apparatus, in colourless transparent crystals. It melts below 100°, and boils at a temperature a little above its melting-point. Its vapour has an intolerably pungent odour, attacks the eyes strongly and painfully, and is excessively poisonous. Osmium tetroxide is dissolved slowly, but in considerable quantity, by water, forming an acid solution. It is a powerful oxidising agent, decolorising indigo-solution, separating iodine from potassium iodide, converting alcohol into aldehyde and acetic acid, etc. It dissolves in alkalis, forming yellow-red solutions, which are inodorous when cold, but when heated, give off the tetroxide and free oxygen, leaving a residue of alkaline osmite.

Sulphides.—Osmium burns in sulphur-vapour. Five sulphides of osmium are said to exist, analogous to the oxides, the first four being produced by decomposing the corresponding chlorides with hydrogen sulphide, and the tetrasulphide by passing that gas into a solution of the tetroxide. The last is a sulphur-acid, perfectly soluble in water, whereas the others are sulphur-bases, slightly soluble in water, and forming deep-yellow solutions.

Ammoniacal Osmium Compounds.—A cold solution of potassium osmite, mixed with sal-ammoniac, yields a yellow crystalline precipitate, consisting, according to Claus, of *hydrated osmammonium chloride*, $Os(NH_3Cl)_2$. An aqueous solution of the tetroxide treated with ammonia yields a brown-black powder, consisting of $N_2H_8OsO_3$, or $O{=}Os{<}\begin{matrix}NH_3OH.\\NH_3OH.\end{matrix}$

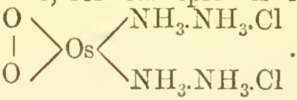
Osmiamic Acid, $H_2Os_2N_2O_5$ or $H_2Os_2N_2O_6$?—The potassium salt of this bibasic acid, $K_2Os_2N_2O_5$, is produced by the action of ammonia on a hot solution of osmium tetroxide in excess of potash:

$$6OsO_4 + 8NH_3 + 6KHO = 3K_2Os_2N_2O_5 + 15H_2O + N_2.$$

It separates as a yellow crystalline powder, and its solution, treated with silver nitrate, yields a precipitate of silver osmiamate, $Ag_2Os_2N_2O_5$, from which the aqueous acid may be prepared by decomposition with hydrochloric acid. It is a strong acid, decomposing not only the carbonates, but also the chlorides, of potassium and sodium. The osmiamates of the alkali-metals and alkaline earth-metals are soluble in water; the lead, mercury, and silver salts are insoluble.

Osmyl-ditetramine Chloride, $OsO_2(NH_3)_4Cl_2$, is obtained as an orange-coloured crystalline precipitate on mixing the concentrated solutions of ammonium chloride and potassium osmate. It is slightly soluble in cold water, but is quickly decomposed by hot water, with evolution of osmium tetroxide and precipitation of a black powder. It dissolves in hot water containing a little hydrochloric acid, forming a deep orange-yellow solution from which it separates on cooling in brown-yellow crystals. It is completely decomposed by ignition, leaving pure metallic osmium as a grey porous mass. The solution of the chloride gives with potassium ferrocyanide a fine violet colour, affording a very delicate test for osmium. The *platinochloride*, $OsO_2(NH_3)_4Cl_2PtCl_4$, forms orange-yellow crystals slightly soluble in cold water. The *sulphate*, $OsO_2(NH_3)_4SO_4$, forms small orange-yellow crystals, freely soluble in hot, slightly in cold water. The *nitrate* forms orange-yellow crystals paler than the sulphate. The *oxalate*, $OsO_2(NH_3)_4C_2O_4$, is a very stable salt, forming yellow or orange-yellow crystals slightly soluble in cold water.

The constitution of the osmyl-ditetramine compounds—the chloride, for example—is most probably represented by the formula



All osmium compounds heated with excess of nitric acid, give off the disagreeable odour of osmium tetroxide. By ignition in hydrogen, they are reduced to metallic osmium, which, as well as the lower oxides, emits the same odour when heated in contact with the air. From solutions of any of its compounds metallic osmium is precipitated by zinc.

PALLADIUM.

Symbol, Pd. Atomic weight, 106·2.

When the solution of crude platinum, from which the greater part of that metal has been precipitated by sal-ammoniac, is neutralised by sodium carbonate, and mixed with a solution of mercuric cyanide, palladium cyanide separates as a whitish insoluble substance, which, on being washed, dried, and heated to redness, yields metallic palladium in a spongy state. The palladium may then be welded into a mass, in the same manner as platinum.

Palladium closely resembles platinum in colour and appearance; it is also very malleable and ductile. Its density differs very much from that of platinum, being only 11·5. It is also much more fusible, its melting-point being about 1500°. Palladium is more oxidisable than platinum. When heated to redness in the air, especially in

the state of sponge, it acquires a blue or purple superficial film of oxide, which is reduced at a white heat. Palladium is slowly attacked by nitric acid ; its best solvent is nitro-muriatic acid.

Palladium, on account of its unalterability in the air, and its bright silver-white colour, which is not affected by exposure to sulphuretted hydrogen, is sometimes used for preparing the graduated surfaces of astronomical instruments, and for coating silver goods.

Palladium is remarkable for its power of occluding hydrogen. When heated to redness in a stream of that gas, or brought into contact with nascent hydrogen, as when made to form the negative electrode in an electrolytic cell containing acidulated water, it can absorb as much as 643 times its volume of the gas, whereby its density is reduced to 11·06. The absorption of the gas is attended with evolution of heat, and the supposed constancy of composition of the hydrogenised palladium has led to the hypothesis that this product is a definite chemical compound ; but this view can scarcely be regarded as satisfactorily demonstrated ; at all events, Graham assigned to the supposed compound the formula PdH_2, whereas, according to Troost and Hautefeuille, it is Pd_2H.

Palladium, like platinum, forms two classes of compounds ; namely, the palladious compounds, *e.g.*, $PdCl_2$ or Pd_2Cl_4, and the palladic compounds, *e.g.*, $PdCl_4$, in which it is quadrivalent.

Chlorides.—*Palladious Chloride*, $PdCl_2$, is obtained by dissolving the metal in nitro-muriatic acid, and evaporating the solution to dryness. It is a dark-brown mass, which dissolves in water if the heat has not been too great, and forms double salts with many metallic chlorides. The palladio-chlorides of ammonium and potassium are much more soluble than the corresponding platino-chlorides : they have a brownish-yellow tint.

The *Tetrachloride*, or *Palladic Chloride*, $PdCl_4$, exists only in solution and in combination with the alkaline chlorides. It is formed when the dichloride is digested in nitro-muriatic acid. The solution has a deep-brown colour, and is decomposed by evaporation. Mixed with potassium chloride, or with sal-ammoniac, it gives rise to a red crystalline precipitate, which is but slightly soluble in water.

Palladious Iodide, PdI_2, is precipitated from the chloride or nitrate by soluble iodides, as a black powder, which gives off its iodine between 300° and 360°. Palladium-salts are sometimes employed for the quantitative estimation of iodine, and its separation from chlorine and bromine, which are not precipitated by them.

Oxides.—*Palladious Oxide*, PdO or Pd_2O_2, is obtained by cautiously heating the nitrate. It is black, and but little soluble in acids. The hydroxide falls as a dark-brown precipitate when sodium carbonate is added to the above solution. It is decomposed by a strong heat.

The *Dioxide*, or *Palladic Oxide*, PdO_2, is not known in the separate state. From a solution of palladic chloride, alkalis and alkaline carbonates throw down a brown precipitate, consisting of hydrated palladic oxide combined with the alkali. This compound gives off half its oxygen at a moderate heat, and the whole at a higher temperature.

Palladious Sulphide, PdS, is formed by fusing the metal with sulphur, or by precipitating a solution of a palladious salt with hydrogen sulphide. It is insoluble in ammonium sulphide.

Ammoniacal Palladium Compounds.—A moderately concentrated solution of palladium dichloride, treated with a slight excess of ammonia, yields a pale-red precipitate, consisting of $N_2H_6PdCl_2$. This precipitate dissolves in a large excess of ammonia ; and the ammoniacal solution, when treated with acids, yields a yellow precipitate having the same composition. This yellow modification is likewise obtained by heating the red compound in the moist state to 100°, or in the dry state to 200°. The yellow compound dissolves abundantly in aqueous potash, forming a yellow solution, but without giving off ammonia, even when the liquid is heated to the boiling-point ; the red compound behaves in a similar manner, but, before dissolving, is converted into the yellow modification. These compounds are analogous in their modes of formation, and probably therefore in constitution, to the two modifications of the platinum compound, $N_2H_6PtCl_2$ (pp. 555, 556) ; the red compound being *palladiosemidiammonium chloride*, $Cl.Pd.NH_2(NH_4)Cl$, and the yellow compound, *palladammonium chloride*, $Pd(NH_3Cl)_2$. The yellow compound, digested with water and silver oxide, yields *palladammonium oxide*, $N_2H_6Pd(OH)_2$, which is a strongly basic substance, soluble in water, having an alkaline taste and reaction, and absorbing carbonic acid from the air. *Palladammonium sulphite*, $N_2H_6PdSO_3$, is formed by the action of sulphurous acid on the oxide or chloride ; it crystallises in orange-yellow octahedrons. The *sulphate*, *chloride*, *iodide*, and *bromide* have likewise been formed.

The compound $(NH_3)_4PdCl_2$, or *Palladiodiammonium chloride*, $Pd[NH_2(NH_4)Cl]_2$, separates from an ammoniacal solution of palladammonium chloride in oblique rhombic prisms.

The *Oxide*, $N_4H_{12}PdO$, obtained by decomposing the solution of this chloride with silver oxide, also yields crystallisable salts.

Palladious salts are well marked by the pale yellowish-white precipitate of palladious cyanide, $PdCy_2$, which they form with solution of *mercuric cyanide*.

Hydriodic acid and *potassium iodide* throw down a black precipitate of palladium iodide, visible even to the 500,000th degree of dilution.

RHODIUM.

Symbol, Rh. Atomic weight, 102·7

The solution from which platinum and palladium have been separated, in the manner already described, is mixed with hydrochloric acid, and evaporated to dryness. The residue is treated with alcohol, of density 0·837, which dissolves everything except the double chloride of rhodium and sodium. This is well washed with spirit, dried, heated to whiteness, and then boiled with water, whereby sodium chloride is dissolved out, and metallic rhodium remains. Thus obtained, rhodium is a white, coherent, spongy mass, still less fusible and less capable of being welded than platinum. Its density is about 12·0.

Rhodium is very brittle: reduced to powder and heated in the air, it becomes oxidised, and the same alteration happens to a greater extent when it is fused with nitrate or bisulphate of potassium. None of the acids, singly or conjoined, dissolve this metal, unless it be in the state of alloy, as with platinum, in which state it is attacked by nitro-muriatic acid.

Rhodium forms but one *chloride*, containing $RhCl_3$ or Rh_2Cl_6, in which, like iron in ferric chloride, it may be regarded as either tri- or quadrivalent. This chloride is prepared by adding silicofluoric acid to the double chloride of rhodium and potassium, evaporating the filtered solution to dryness, and dissolving the residue in water. It forms a brownish-red deliquescent mass, soluble in water, with a fine red colour. It is decomposed by heat into chlorine and metallic rhodium.

Rhodium and Potassium Chlorides.—The salt, $K_6Rh_2Cl_{12}6H_2O$, formed by mixing a solution of rhodic oxide in hydrochloric acid with a strong solution of potassium chloride, crystallises in sparingly soluble efflorescent prisms. Another double salt, containing $K_4Rh_2Cl_{10},2H_2O$, is prepared by heating in a stream of chlorine a mixture of equal parts of finely powdered metallic rhodium and potassium chloride. The salt has a fine red colour, is soluble in water, and crystallises in four-sided prisms. *Rhodium and sodium chloride*, $Na_6Rh_2Cl_{12},24H_2O$, is also a very beautiful red salt, prepared like the last. The *ammonium salt*, $(NH_4)_6Rh_2Cl_{12},3H_2O$, obtained by decomposing the sodium salt with sal-ammoniac, crystallises in fine rhombohedral prisms.

Rhodium Oxides. — Rhodium forms four oxides, containing RhO, Rh_2O_3, RhO_2, and RhO_3.

The *Monoxide*, RhO or Rh_2O_2, is formed with incandescence, when the hydrated sesquioxide, $Rh_2O_3,3H_2O$, is heated in a platinum crucible. It is a dark-grey substance, perfectly indifferent to acids.

The *Sesquioxide*, or *Rhodic Oxide*, Rh_2O_3, obtained by heating the nitrate, is a grey porous mass, with metallic iridescence; insoluble in acids, easily reduced by hydrogen.

The *Trihydroxide*, or *Rhodic Hydroxide*, $Rh_2(OH)_6$, is formed as a black gelatinous precipitate on heating a solution of sodio-rhodic chloride with caustic potash. When dry it forms a heavy dark-brown metallically lustrous mass having a conchoïdal fracture. It is scarcely attacked by acids. A solution of sodio-rhodic chloride treated with potash in the cold, becomes opaque, and after some time deposits thin lemon-yellow crystals of the hydrate $Rh_2(OH)_6, 2H_2O$, which dissolves readily in acids, and when moist in caustic potash.

The *Dioxide*, RhO_2, obtained by fusing pulverised rhodium or the sesquioxide with nitre and potash, and digesting the fused mass with nitric acid, to dissolve out the potash, is a dark-brown substance insoluble in acids. It may also be obtained by treating the trihydrate, $Rh_2O_3,3H_2O$, with chlorine. This compound gradually loses its gelatinous consistence, becomes lighter in colour, and is finally converted into a green hydrate of the dioxide, $RhO_2,2H_2O$. The alkaline solution at the same time acquires a deep violet-blue colour.

The *Tetrahydroxide*, $Rh(OH)_4$, separates on passing chlorine for a long time into an alkaline solution of the trihydroxide, with occasional addition of potash, in the form of a blue powder, the liquid at the same time assuming a blue or violet tint. The blue powder dissolves in hydrochloric acid, yielding a blue solution gradually changing to dark red, with evolution of chlorine. The violet-blue solution probably contains the potassium salt of a *rhodic acid*, which latter separates after some time as a blue powder, and is converted on drying into the tetrahydroxide.

Rhodic Sulphate, $Rh_2(SO_4)_3 12H_2O$, formed by oxidising the sulphide with nitric acid, is a yellowish-white crystalline mass. *Potassio-rhodic sulphate*, $RhK_3(SO_4)_3$, is a reddish-yellow crystalline powder, formed by adding sulphuric acid to a solution of rhodium and potassium chloride.

Ammoniacal Rhodium Compounds. — An *ammonio-chloride*, $(NH_3)_{10}Rh_2Cl_6$, or $Cl(NH_3)_5—RCl_2—RCl_2—(NH_3)_5—Cl$, is obtained as a yellow crystalline powder on mixing a dilute solution of rhodium and ammonium chloride with excess of ammonia, and leaving the filtered solution to evaporate. The corresponding oxide, $(NH_3)_{10}Rh_2O_3$, obtained by heating the chloride with silver oxide, is a strongly basic substance, from which the sulphate and oxalate may be obtained in crystalline form.

Rhodic salts are, for the most part, rose-coloured, and exhibit in solution the following reactions: with *hydrogen sulphide* and *ammonium sulphide*, a brown precipitate of rhodic sulphide, insoluble in excess of ammonium sulphide: with soluble *sulphites*, a pale-yellow precipitate, affording a characteristic reaction; with *potash*, a yellow precipitate of rhodic oxide, soluble in excess; with *ammonia*

and with *alkaline carbonates*, a yellow precipitate after a while. No precipitate with alkaline chlorides or mercuric cyanide. *Zinc* precipitates metallic rhodium as a black powder.

RUTHENIUM.

Symbol, Ru. Atomic weight, 101·4.

This metal, discovered by Claus in 1846, occurs in platinum ore, and chiefly in osmiridium, of which there are two varieties—one scaly, consisting almost wholly of osmium, iridium, and ruthenium ; while the other, which is granular, contains but mere traces of osmium and ruthenium, but is very rich in iridium and rhodium. To obtain ruthenium, scaly osmiridium is heated to bright redness in a porcelain tube, through which a current of air is drawn by means of an aspirator. The osmium and ruthenium are thereby oxidised, the former being carried forward as tetroxide and condensed in caustic potash solution, while the ruthenium oxide remains behind, together with iridium ; and by fusing this residue with potassium hydroxide, treating the mass with water, and leaving the liquid in a bottle for about two hours to clarify, an orange-coloured solution of potassium rutheniate is obtained, which, when neutralised with nitric acid, deposits velvet-black ruthenium sesquioxide, and this, when washed, dried, and ignited in hydrogen, yields the metal.

Ruthenium, thus prepared, forms porous lumps very much like iridium, and is moderately easy to pulverise. It is the most refractory of all metals except osmium, but it may be melted in the electric furnace. After fusion its density is 12·06 ; that of the porous metal is much less.

Ruthenium is scarcely attacked by nitro-muriatic acid. It is, however, more easily oxidised than platinum, or even than silver. When pure it is easily oxidised by fusion with potassium hydroxide, still more easily on addition of a small quantity of nitrate or chlorate, producing potassium rutheniate, which dissolves in water with orange-yellow colour.

Chlorides.—Ruthenium forms two chlorides, $RuCl_2$ and $RuCl_3$.

Ruthenious chloride, $RuCl_2$ or Ru_2Cl_4, is produced, together with the ruthenic chloride, by igniting pulverised ruthenium in a stream of chlorine, the higher chloride then volatilising, while the lower chloride remains in the form of a black crystalline powder, insoluble in water and in all acids, even nitro-muriatic acid, and only partially decomposed by alkalis.

Ruthenic Chloride, $RuCl_3$ or Ru_2Cl_6, prepared by precipitating a solution of potassic rutheniate with an acid, dissolving the precipitated black oxide in hydrochloric acid, and evaporating, is a yellow-brown, crystalline, very deliquescent mass.

The concentrated solution of ruthenic chloride, mixed with concentrated solutions of the chlorides of potassium and ammonium, yields the double salts, $4KCl.Ru_2Cl_6$ and $4NH_4Cl.Ru_2Cl_6$, in the form of crystalline precipitates, with violet iridescence, very slightly soluble in water, insoluble in alcohol.

Oxides.—Ruthenium forms six oxides, viz., RuO, Ru_2O_3, RuO_2, RuO_3, Ru_2O_7, and RuO_4, the fourth and fifth, however, being known only in combination.

The *Monoxide*, RuO or Ru_2O_2, obtained by calcining the dichloride with sodium carbonate in a current of carbon dioxide, and washing the residue with water, has a dark-grey colour and metallic lustre; is not acted upon by acids; but is reduced by hydrogen at ordinary temperatures.—*Ruthenic Oxide*, Ru_2O_3, is a bluish-black powder, formed by heating the metal in the air. The corresponding hydroxide, $Ru(OH)_3$, is obtained by precipitating ruthenious chloride with an alkaline carbonate, as a blackish-brown substance which dissolves with yellow colour in acids. The *Dioxide*, or *Ruthenic Oxide*, RuO_2, is a blue-black powder, obtained by roasting the disulphide. *Ruthenic Hydroxide*, $Ru(OH)_4$, is obtained as a gelatinous precipitate by decomposing potassium chlororutheniate with sodium carbonate.—The *Trioxide*, RuO_3, commonly called *Ruthenic Acid*, is known only as a potassium salt, K_2RuO_4, which is obtained by igniting ruthenium with caustic potash and nitre: it forms an orange-yellow solution.—The *Oxide*, Ru_2O_7, called *Ruthenium Peroxide*, is not known in the free state, neither has the corresponding acid, "per-ruthenic acid," been obtained; but the potassium salt is formed by the action of chlorine on potassium ruthenate, and separates from the resulting dark-green solution in black lustrous rhombic pyramids, isomorphous with potassium permanganate. The blackish-green solution soon turns yellow, being resolved into potassium ruthenate and the following oxide.—The *Tetroxide*, RuO_4, is a volatile compound, analogous to osmic tetroxide, obtained by heating ruthenium with potash and nitre, in a silver crucible, dissolving the fused mass in water, and passing chlorine through the solution in a tubulated retort, connected by a condensing tube with a receiver containing potash. The tetroxide then passes over and condenses in the neck of the retort and in the tube, as a golden-yellow crystalline crust, which melts at 25·5°. It is heavier than oil of vitriol, dissolves slightly in water, readily in hydrochloric acid, forming a solution easily decomposed by alcohol, sulphurous acid, and other reducing agents.

Sulphides.—Hydrogen sulphide, passed into a solution of either of the chlorides of ruthenium, usually forms a precipitate consisting of ruthenium sulphide and oxysulphide mixed with free sulphur. The blue solution of the dichloride yields a dark-brown sesquisulphide, Ru_2S_3. When hydrogen sulphide is passed for a long time into a solution of the trichloride, ruthenium disulphide, RuS_2, is

formed, as a brown-yellow precipitate, becoming dark-brown by calcination.

Ammoniacal Ruthenium Compounds.—Several compounds have been obtained corresponding in general characters with the ammoniacal compounds of rhodium, but they require further investigation, as authorities differ concerning their composition.

The compounds of ruthenium may readily be distinguished from those of the other platinum-metals, by fusing a few milligrams of the substance in a platinum spoon, with a large excess of nitre, leaving it to cool when it ceases to froth, and dissolving the cooled mass in a little distilled water. An orange-yellow solution of potassium rutheniate is thus formed, which on addition of a drop or two of nitric acid yields a bulky, black precipitate; and on adding hydrochloric acid to the liquid, with the precipitate still in it, and heating it in a porcelain crucible, the oxide dissolves, forming a solution which has a fine orange-yellow colour when concentrated, and when treated with *hydrogen sulphide* till it becomes nearly black, yields a filtrate of a splendid sky-blue colour. Characteristic reactions are also obtained with *potassium thiocyanate*, which colours the liquid deep red, changing to violet on heating, and with *lead acetate*, which forms a purple-red precipitate.

APPENDIX.

USEFUL TABLES

Table I.

ABSTRACT

Of Regnault's Table of the Maximum Tension of Water-Vapour at different Temperatures, expressed in Millimeters of Mercury.

Temperature.	Tension millimeters.	Temperature.	Tension millimeters.
− 32° C.	0·320	100° C.	760·000
30	0·386	105	906·410
25	0·605	110	1075·370
20	0·927	115	1269·410
15	1·400	120	1491·280
10	2·093	125	1743·880
5	3·113	130	2030·280
0	4·600	135	2353·730
+ 5	6·534	140	2717·630
10	9·165	145	3125·55
15	12·699	150	3581·23
20	17·391	155	4088·56
25	23·550	160	4651·62
30	31·548	165	5274·54
35	41·827	170	5961·66
40	54·906	175	6717·43
45	71·391	180	7546·39
50	91·982	185	8453·23
55	117·478	190	9442·70
60	148·791	195	10519·63
65	186·945	200	11688·96
70	233·093	205	12955·66
75	288·517	210	14324·80
80	354·643	215	15801·33
85	433·041	220	17390·36
90	525·450	225	19097·04
95	633·778	230	20926·40

TABLE II.

WEIGHT OF ONE CUBIC CENTIMETER OF ATMOSPHERIC AIR, IN GRAMS, AT DIFFERENT TEMPERATURES, FOR EVERY 5 DEGREES FROM 0° TO 300° C. AT 760 MM.

		Difference.			Difference.
0°	0·001293	23	155°	0·000824	9
5	0·001270	22	160	0·000815	9
10	0·001248	22	165	0·000806	9
15	0·001226	21	170	0·000797	9
20	0·001205	20	175	0·000788	9
25	0·001185	20	180	0·000779	9
30	0·001165	19	185	0·000770	8
35	0·001146	18	190	0·000762	8
40	0·001128	17	195	0·000754	8
45	0·001111	17	200	0·000746	8
50	0·001094	17	205	0·000738	8
55	0·001077	17	210	0·000730	8
60	0·001060	16	215	0·000722	7
65	0·001044	15	220	0·000715	7
70	0·001029	15	225	0·000708	7
75	0·001014	14	230	0·000701	7
80	0·001000	14	235	0·000694	7
85	0·000986	14	240	0·000687	7
90	0·000972	13	245	0·000680	6
95	0·000959	13	250	0·000674	6
100	0·000946	13	255	0·000668	6
105	0·000933	12	260	0·000662	6
110	0·000921	12	265	0·000656	6
115	0·000909	11	270	0·000650	6
120	0·000898	11	275	0·000644	6
125	0·000887	11	280	0·000638	6
130	0·000876	11	285	0·000632	6
135	0·000865	11	290	0·000626	5
140	0·000854	10	295	0·000621	5
145	0·000844	10	300	0·000616	
150	0·000834				

The column of Differences is intended to facilitate the calculation of the intermediate values. Thus to find the weight of 1 cub. cent. of air for 52°, we must deduct from the weight for 50°, two-fifths of the difference (17) between this and the number for 55 degrees: thus—

Weight of 1 cub. cent. of air at 50°	=	0·001094
Deduct $\frac{2}{5}$ of 17 ,, ,,	=	7
Weight of 1 cub. cent. of air at 55°	=	0·001087

Table III.

For the Calculation of $\frac{1}{1+0{\cdot}00367t}$. (*See page* 49.)

t		t		t		t		t	
1	0·99634	31	0·89785	61	0·81708	91	0·74964	121	0·69249
2	0·99271	32	0·89490	62	0·81464	92	0·74758	122	0·69073
3	0·98911	33	0·89197	63	0·81221	93	0·74554	123	0·68899
4	0·98553	34	0·88906	64	0·80979	94	0·74351	124	0·68725
5	0·98198	35	0·88617	65	0·80740	95	0·74148	125	0·68552
6	0·97845	36	0·88330	66	0·80501	96	0·73947	126	0·68380
7	0·97495	37	0·88044	67	0·80264	97	0·73747	127	0·68209
8	0·97148	38	0·87761	68	0·80068	98	0·73548	128	0·68038
9	0·96803	39	0·87479	69	0·79794	99	0·73350	129	0·67869
10	0·96460	40	0·87199	70	0·79561	100	0·73153	130	0·67700
11	0·96120	41	0·86921	71	0·79329	101	0·72957	131	0·67532
12	0·95782	42	0·86645	72	0·79099	102	0·72765	132	0·67365
13	0·95446	43	0·86370	73	0·78870	103	0·72568	133	0·67199
14	0·95113	44	0·86097	74	0·78642	104	0·72376	134	0·67034
15	0·94782	45	0·85826	75	0·78416	105	0·72184	135	0·66870
16	0·94454	46	0·85556	76	0·78191	106	0·71993	136	0·66706
17	0·94127	47	0·85289	77	0·77967	107	0·71803	137	0·66543
18	0·93803	48	0·85022	78	0·77745	108	0·71615	138	0·66380
19	0·93482	49	0·84758	79	0·77523	109	0·71427	139	0·66219
20	0·93162	50	0·84495	80	0·77304	110	0·71240	140	0·66059
21	0·92844	51	0·84234	81	0·77085	111	0·71055	141	0·65899
22	0·92529	52	0·83974	82	0·76867	112	0·70870	142	0·65740
23	0·92216	53	0·83716	83	0·76651	113	0·70686	143	0·65582
24	0·91905	54	0·83460	84	0·76436	114	0·70503	144	0·65424
25	0·91596	55	0·83205	85	0·76222	115	0·70321	145	0·65268
26	0·91289	56	0·82952	86	0·76010	116	0·70140	146	0·65112
27	0·90984	57	0·82700	87	0·75798	117	0·69960	147	0·64957
28	0·90682	58	0·82450	88	0·75588	118	0·69781	148	0·64802
29	0·90381	59	0·82201	89	0·75379	119	0·69603	149	0·64648
30	0·90082	60	0·81954	90	0·75171	120	0·69425	150	0·64495

Table IV.

WEIGHTS AND MEASURES.

480	grains Troy	=1 oz. Troy.
437·5	„	=1 oz. Avoirdupois.
7000	„	=1 lb. Avoirdupois.
5760	„	=1 lb. Troy.

The imperial gallon contains of water at 62° F. ($16\frac{2}{3}$° C.)	70,000 grains.
The pint ($\frac{1}{8}$ of gallon), ...	8,750 „
The fluid ounce ($\frac{1}{20}$ of pint), ...	437·5 „

The pint equals 34·56 cubic inches.

METRIC SYSTEM.

Names of units :—

Length, ... Meter = 39·37 inches
Volume, ... Litre = 1·76 pint
(or 1 cubic decimeter).
Weight, ... Gram = 15·43 grains.
(Mass of 1 cubic centimeter of water at 4°.)

Meaning of prefixes to names of units :—

Myria, ...	10,000
Kilo, ...	1,000
Hecto, ...	100
Deka, ...	10
Deci, ...	·1 or $\frac{1}{10}$
Centi, ...	·01 or $\frac{1}{100}$
Milli, ...	·001 or $\frac{1}{1000}$

Example :—1 Kilogram = 1000 grams.
1 Decimeter = $\frac{1}{10}$ of a meter.

For complete comparison of English and Metric Weights and Measures, see tables on next two pages.

TABLE V.—COMPARISON OF FRENCH AND ENGLISH MEASURES. By Warren De La Rue.

MEASURES OF LENGTH.

	In English Inches.	In English Feet =12 Inches.	In English Yards =3 Feet.	In English Fahms. =6 Feet.	In English Miles =1760 Yards.
Millimeter, ...	0·03937	0·0032809	0·0010936	0·0005468	0·0000006
Centimeter, ...	0·39371	0·0328090	0·0109363	0·0054682	0·0000062
Decimeter, ...	3·93708	0·3280899	0·1093633	0·0546816	0·0000621
Meter, ...	39·37079	3·2808992	1·0936331	0·5468165	0·0006214
Decameter, ...	393·70790	32·8089920	10·9363310	5·4681655	0·0062138
Hectometer, ...	3937·07900	328·0899200	109·3633100	54·6816550	0·0621382
Kilometer, ...	39370·79000	3280·8992000	1093·6331000	546·8165500	0·6213824
Myriameter, ...	393707·90000	32808·9920000	10936·3310000	5468·1655000	6·2138244

1 Inch = 2·539954 Centimeters.
1 Foot = 3·0479449 Decimeters.

1 Yard = 0·91438348 Meter.
1 Mile = 1·6993149 Kilometer.

MEASURES OF SURFACE.

	In English Square Feet.	In English Sq. Yds. =9 Square Feet.	In English Poles =272·25 Sq. Feet.	In English Roods =10,890 Sq. Feet.	In English Acres =43,560 Sq. Feet.
Centiare or Square Meter, . .	10·7642993	1·1960333	0·0395383	0·000988457	0·0002471143
Are or 100 Square Meters, . .	1076·4299342	119·6033260	3·9538290	0·098845724	0·0247114310
Hectare or 10,000 Square Meters, .	107642·9934183	11960·3326020	395·3828959	9·884572398	2·4711430996

1 Square Inch = 6·4513669 Square Centimeters.
1 Square Foot = 9·2899683 Square Decimeters.

1 Square Yard = 0·83609715 Square Meter or Centiare.
1 Acre = 0·401671021 Hectare.

TABLE V. (*continued*).—MEASURES OF CAPACITY.

	In Cubic Inches.	In Cubic Feet =1728 Cubic Inches.	In Pints =34·65923 Cubic Inches.	In Gallons = 8 Pints=277·27384 Cubic Inches.	In Bushels=8 Gallons=2218·19075 Cubic Inches.
Millilitre, or Cubic Centimeter, .	0·061027	0·0000353	0·001761	0·00022010	0·000027512
Centilitre, or 10 Cubic Centimeters,	0·610271	0·0003532	0·017608	0·00220097	0·000275121
Decilitre, or 100 Cubic Centimeters,	6·102705	0·0035317	0·176077	0·02200967	0·002751208
Litre, or Cubic Decimeter, . .	61·027052	0·0353166	1·760773	0·22009668	0·027512085
Decalitre, or Centistere, . .	610·270515	0·3531658	17·607734	2·20096677	0·275120846
Hectolitre, or Decistere, . .	6102·705152	3·5316581	176·077341	22·00966767	2·751208459
Kilolitre, or Stere or Cubic Meter, .	61027·051519	35·3165807	1760·773414	220·09667675	27·512084594
Myrialitre, or Decastere, . .	610270·515194	353·1658074	17607·734140	2200·96676750	275·120845937

1 Cubic Inch=16·3861759 Cubic Centimeters. 1 Cubic Foot=28·3153119 Cubic Decimeters. 1 Gallon=4·543457969 Litres.

MEASURES OF WEIGHT.

	In English Grains.	In Troy Ounces =480 Grains.	In Avoirdupois lbs.=7000 Grains.	In Cwts.=112 lbs. =784,000 Grains.	Tons=20 Cwts. =15,680,000 Grains.
Milligram, ...	0·015432	0·000032	0·0000022	0·00000002	0·000000001
Centigram, ...	0·154323	0·000322	0·0000220	0·00000020	0·000000010
Decigram, ...	1·543235	0·003215	0·0002205	0·00000197	0·000000098
Gram, ...	15·432349	0·032151	0·0022046	0·00001968	0·000000984
Decagram, ...	154·323488	0·321507	0·0220462	0·00019684	0·000009842
Hectogram, ...	1543·234880	3·215073	0·2204621	0·00196841	0·000098421
Kilogram, ...	15432·348800	32·150727	2·2046213	0·01968412	0·000984206
Myriagram, ...	154323·488000	321·507267	22·0462126	0·19684118	0·009842059

1 Grain=0·064798950 Gram. 1 Troy oz.=31·103496 Gram. 1 lb. Avd.=0·45359265 Kilogr. 1 Cwt.=50·80237689 Kilog.

Table VI.

For Converting Degrees of the Centigrade Thermometer into Degrees of Fahrenheit's Scale.

Centigrade.	Fahrenheit.	Centigrade.	Fahrenheit.	Centigrade.	Fahrenheit.
−90°	−130°	−60°	−76°	−30°	−22°
85	121	55	67	25	13
80	112	50	58	20	4
75	103	45	49	15	+ 5
70	94	40	40	10	14
65	85	35	31	5	23
0°	+32°	+100°	+212°	+200°	392°
+ 5	41	105	221	205	401
10	50	110	230	210	410
15	59	115	239	215	419
20	68	120	248	220	428
25	77	125	257	225	437
30	86	130	266	230	446
35	95	135	275	235	455
40	104	140	284	240	464
45	113	145	293	245	473
50	122	150	302	250	482
55	131	155	311	255	491
60	140	160	320	260	500
65	149	165	329	265	509
70	158	170	338	270	518
75	167	175	347	275	527
80	176	180	356	280	536
85	185	185	365	285	545
90	194	190	374	290	554
95	203	195	383	295	563

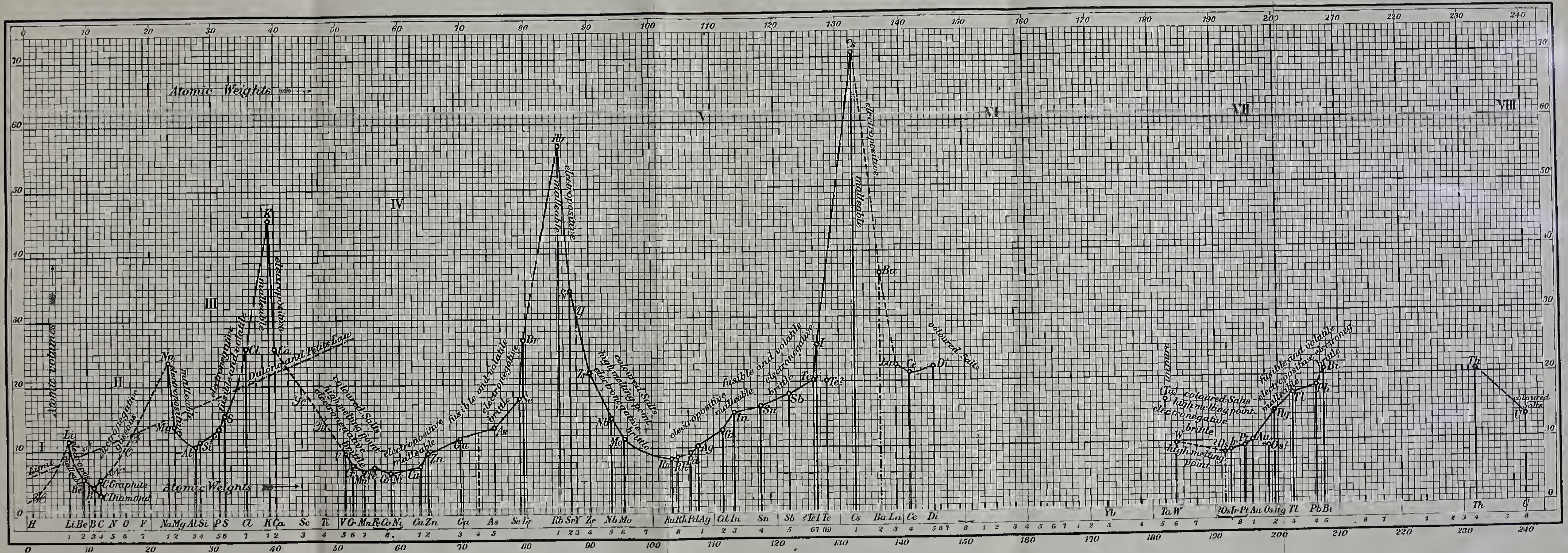
$$5^\circ \text{ C.} = 9^\circ \text{ F.}$$

To convert C. into F. temperatures,

$$\frac{\text{C.} \times 9}{5} + 32 = \text{F.}$$

To convert F. into C.,

$$\text{F.} - 32 \times \frac{5}{9} = \text{C.}$$



Whiteman & Bass, Litho London.

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